POCP for individual VOC under European conditions

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Sammanfattning/Summary

Ground level ozone has been recognised as one of the most important environmental threats on the regional scale in Europe. Ozone is today considered to be harmful to human health already at the relatively low concentrations present in southern Scandinavia. The fact that ozone has the potential to damage vegetation at these concentrations is already well known. Ozone also gives rise to degradation of materials and is one of the gases which adds to the greenhouse effect.

Ground level ozone is formed from nitrogen oxides (NO_x) and volatile organic compounds (VOC) in the presence of sunlight. The only way to reduce ozone is therefore to reduce the emissions of the precursors. Ranking individual VOC by their ozone formation potential can make emission reductions more environmentally efficient and save time and money. POCP values give a ranking of the ozone formation ability of an individual VOC relative to other VOC.

A critical analysis of the POCP concept has been performed which shows that the background emissions of NO_x and VOC affect the POCP values to a large extent. Based on the critical analysis, five scenarios with different background emissions of NO_x and VOC were selected for calculation of POCP values. These scenarios were chosen because they reflect the variation in POCP values which arise in different environments within Europe. The range thus indicates POCP values which are intended to be applicable within Europe. POCP values for 83 different VOC are presented in the form of ranges in this report.

Nyckelord samt ev. anknytning till geografiskt område, näringsgren eller vattendrag/Keywords

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Sammanfattning

Marknära ozon är ett av de viktigaste miljöhoten på regional skala i Europa. Ozon anses idag vara skadligt för hälsan redan vid de relativt låga koncentrationer som förekommer i södra Skandinavien. Att ozon också skadar växtlighet vid dessa koncentrationer är numera välkänt. Ozon påskyndar dessutom åldrandet hos olika material och är en av de gaser som bidrar till växthuseffekten.

Marknära ozon bildas från kväveoxider (NO_x) och flyktiga organiska ämnen (VOC, Volatile Organic Compounds) under inverkan av solljus. Det enda sättet att minska halterna av marknära ozon är därför att minska emissionerna av NO_x och VOC. Olika VOC skiljer sig åt vad gäller deras förmåga att bilda ozon. Den absoluta mängd ozon som bildas från ett visst utsläpp varierar också kraftigt beroende på den rådande luftmiljön och meteorologin där utsläppet sker. Genom att rangordna VOC efter deras ozonbildningsförmåga kan emissionsminskningar göras mer miljömössigt effektiva och samtidigt spara tid och pengar.

Beräkning av POCP-värden (POCP, Photochemical Ozone Creation Potential) är en metod att rangordna förmågan att bilda ozon hos olika VOC. POCP-värdet ger ett mått på ozonbildningsförmågan hos ett enskilt VOC, relativt andra VOC.

För att erhålla användbara POCP-värden för europeiska förhållanden har en kritisk analys av POCP-konceptet utförts. Främst har förändringar i den relativa ozon-bildningen från olika VOC undersökts då miljön förändras. Olika miljöer med kemiska och meteorologiska förhållanden som är representativa för Europa har studerats. Studien har utförts med hjälp av IVLs fotokemiska trajektoriemodell.

Den kritiska analysen visar att bakgrundsemissionerna av NO_x och VOC påverkar de relativa POCP-värdena i hög grad. Övriga modellparametrar som studerats (t.ex. depositionshastigheter, temperatur, bakgrundsemissioner av CH_4) har inte visat lika stor påverkan på POCP-värdena och dessa parametrar har därför ansatts baserat på resultaten från den kritiska analysen.

Fem scenarier med olika bakgrundsemissioner av NO_x och VOC har använts för att beräkna POCP-värden. Dessa scenarier har valts ut för att spegla den variation i POCP-värden som uppkommer i olika miljöer inom Europa. Intervallet anger därmed POCP-värden som är avsedda att tillämpas inom Europa. POCP-värden för 83 olika VOC redovisas i form av intervall i denna rapport.

I många praktiska situationer står valet mellan utsläppsminskningar av VOC kontra NO_x. Beräkningar av ozonbildningen från ett utsläpp bestående av en blandning av olika VOC redovisas därför jämte motsvarande utsläpp av NO_x (baserat på samma antal kg) för 25 olika scenarier med olika bakgrundsemissioner av NO_x och VOC.

De beräknade POCP-värdena för 83 olika VOC presenteras i Kapitel 6 tillsammans med en generell genomgång av hur NO_x och VOC kan prioriteras i förhållande till varandra. Den kritiska analysen av POCP-begreppet, som föregått beräkningarna av POCP-intervall, beskrivs i Kapitel 2, 3 och 4.

Summary

Ground level ozone has been recognised as one of the most important environmental threats on the regional scale in Europe. Ozone is today considered to be harmful to human health already at the relatively low concentrations present in southern Scandinavia. The fact that ozone has the potential to damage vegetation at these concentrations is already well known. Ozone also gives rise to degradation of materials and is one of the gases which adds to the greenhouse effect.

Ground level ozone is formed from nitrogen oxides (NO_x) and volatile organic compounds (VOC) in the presence of sunlight. The only way to reduce ozone is therefore to reduce the emissions of the precursors. Different VOC vary in their ability to produce ozone. The absolute production of ozone from a certain emission also varies substantially depending on the air quality and meteorology where the emission is released. Ranking individual VOC by their ozone formation potential can make emission reductions more environmentally efficient and save time and money.

The calculation of Photochemical Ozone Creation Potentials (POCP) is one method to rank the ability to produce ozone from individual VOC. The POCP values give a ranking of the ozone formation ability of an individual VOC relative to other VOC.

To obtain POCP values valid under European conditions, a critical analysis of the POCP concept has been performed. The study has mainly investigated the changes in relative POCP values for different VOC due to changes in the environment. Different environments with chemical and meteorological conditions representative for Europe have been studied. The study has been performed using the IVL photochemical trajectory model.

The critical analysis shows that the background emissions of NO_x and VOC affect the POCP values to a large extent. Other model parameters which have been studied (e.g. deposition velocities, temperature, background emissions of CH_4) have not shown such large influence on the POCP values and therefore these parameters have been set based on the results from the critical analysis.

Five scenarios with different background emissions of NO_x and VOC were used for calculation of POCP values. These scenarios have been chosen to reflect the variation in POCP values which arise in different environments within Europe. The range thus indicates POCP values which are intended to be applicable within Europe. POCP values for 83 different VOC are presented in the form of ranges in this report.

In many real life situations the choice stands between reducing the emissions of VOC or NO_x. The results from calculations of the ozone formation from an emission of a mixture of VOC or from an equally large emission of NO_x (by weight) in 25 different scenarios with different background emissions of NO_x and VOC are therefore given.

The calculated POCP values for 83 different VOC are presented in Chapter 6 together with a general description of how to chose between NO_x or VOC emission reductions in order to reduce ozone. The critical analysis of the POCP concept is presented in Chapters 2, 3 and 4.

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1   Introduction

1.1   *Environmental impacts of VOC in the atmosphere*

When Volatile Organic Compounds (VOC) are emitted to the atmosphere they influence the environment and our health in many different ways. VOC may cause effects on human health, plants and animals and also on the climate of the earth.

The direct negative effects on human health from VOC are local, mainly of concern close to the emission sources and in working environments, since it is only in these places that high concentrations of VOC are reached. The atmospheric degradation of VOC will cause production of ozone and other photooxidants on the regional scale in the presence of NO_x and sunlight. Chlorinated VOC may bioaccumulate or may survive long enough to reach the stratosphere where they may contribute to the ozone depletion. Some VOC may act as greenhouse gases and thus add to the global warming. The final products of the atmospheric degradation of VOC are CO_2 and water. All emissions of VOC from fossil origin will contribute to the greenhouse effect since they cause fossil carbon to be transformed to CO_2 in the atmosphere.

This report will focus on the production of ozone from VOC and will not deal with other environmental or health effects caused by VOC in the atmosphere. The reader is however reminded that there are other aspects than the formation of ozone to be considered in the choice between different VOC, as mentioned above.

1.2   *Tropospheric ozone*

Tropospheric ozone, or ground level ozone, has been recognised as one of the most important environmental threats on the regional scale. At high concentrations it is hazardous to human health, but already at lower concentrations it causes damage to vegetation. It also gives rise to degradation of materials as well as adds to the greenhouse effect.

In the US, the high concentrations of ground level ozone, which occur in and around large cities like Los Angeles, cause human health problems. Since traffic is the largest source of emissions of NO_x and VOC, many requirements have been directed towards the automotive industry to come up with alternatively fuelled vehicles and electrical vehicles. The increase in health costs for high levels of tropospheric ozone in LA have been estimated to be around 9 billion US dollars (70 bill. sek) (Ljungqvist, 1995).

In Europe, there are also severely polluted areas which suffer from smog and high levels of tropospheric ozone. Efforts are made all over Europe to deal with the ozone problem both on a European and a local scale. Some examples are speed limits which have been introduced in Germany (Carlsson, 1995), and different measures implemented to promote public transportation on a local level in both France and Great Britain (Munther, 1997; Ericsson, 1997). Within the framework of the convention on transboundary air pollution (UNECE/LRTAP nitrogen protocols), the ozone problem is a topic of highest priority together with acidification.

The health problems caused by ozone have generally been considered to be an effect of the very high peaks of ozone concentration, known as ozone episodes (Lefohn, 1997). Increased background levels of ozone also cause problems since it is proven to cause damage to vegetation (Heck *et al.*, 1988; Skärby *et al.*, 1993; Sandermann *et al.*, 1997).

In Europe (within the UNECE work on a new NO_x protocol) the so called critical level AOT40 (Accumulated exposure Over Threshold 40 ppb) is used to describe ozone damages to vegetation. AOT40 is an accumulated value given in ppb·hours and is calculated as the sum of the exceedence of the ozone concentration above 40 ppb for daylight hours. Ozone levels below 40 ppb are not included in AOT40.

1.3 *The photostationary state*

Ground level ozone is formed from nitrogen oxides (NO_x) and VOC under the influence of sunlight. The reaction which produces ozone (O_3) in the troposphere is the photolysis of nitrogen dioxide (NO_2), which produces nitric oxide (NO) and atomic oxygen (O). Atomic oxygen combines with an oxygen molecule (O_2) to form ozone. Ozone can oxidise nitric oxide to nitrogen dioxide and together these reactions form a steady state between ozone, nitric oxide and nitrogen dioxide referred to as the photostationary state (reactions 1-3). Species M in reaction 2 represents an unreactive molecule (often N_2, a nitrogen molecule) which is not affected by the reaction .

$$NO_2 + h\nu \ \rightarrow \ NO + O \qquad\qquad (1)$$
$$O + O_2 + M \ \rightarrow \ O_3 + M \qquad\qquad (2)$$
$$NO + O_3 \ \rightarrow \ NO_2 + O_2 \qquad\qquad (3)$$
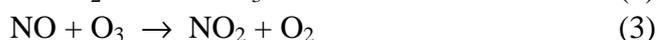
If no VOC were present in the atmosphere, the photostationary state would govern the background levels of ozone. When VOC are introduced into the troposphere they are oxidised to produce peroxy radicals. Peroxy radicals can either consume NO or convert it to NO_2 and compete with ozone in the photostationary state. Less ozone is thereby destroyed through the reaction with NO (reaction 3) and hence the ozone concentration increases.

1.4 *NO_x and VOC, the precursors of tropospheric ozone*

NO_x is not consumed in the photostationary state but is regenerated and thus acts as a catalyst (reactions 1-3). Organic compounds, on the other hand, act as the fuel for ozone production and are consumed in the process. NO_x still has a shorter lifetime in the atmosphere than most organic species. NO_x is removed from the atmosphere by deposition of nitrogen oxides and of organic nitrate compounds formed from reactions between NO_x and VOC.

It is usually referred to two different states of the chemistry in the atmosphere, the low NO_x and the high NO_x regimes (Lin *et al.*, 1988; Kleinman, 1994). In the low NO_x regime, the production of ozone is mainly governed by the amount of available NO_x, while in the high NO_x regime, the amount of ozone which is produced is controlled

both by the NO_x and VOC levels (Sillman *et al.*, 1990). Urban areas are generally in the high NO_x regime while rural areas are in the low NO_x regime. The transition between the two regimes is wide and therefore it is not possible to classify all different air masses as being strictly in the low or in the high NO_x regime. As an air mass is transported with the wind over the ground, the chemical composition changes as new emissions are released and chemical reactions take place. The status of an air mass may thus easily change from one NO_x regime to the other along its path.

The only way to reduce ground level ozone is to decrease the emissions of the precursors. Either of the two precursors, NO_x and VOC, or a combination of both will limit the rate of ozone production. The emissions in Europe can vary greatly from one area to another and sometimes areas of different NO_x regimes are in close vicinity of each other (Barrett and Berge, 1996). This makes abatement strategy work difficult and the reduction strategies towards ozone in Europe have therefore generally focused on the question of NO_x versus VOC control.

Emission reductions can be both time consuming and expensive, and an optimised strategy to give the highest possible ozone reduction per effort and money spent on control measures is therefore needed. In the high NO_x regime, where the emissions are generally high of both NO_x and VOC, the best way to reduce ozone is to decrease the VOC emissions (Altshuler *et al.*, 1995). Since VOC differ in their ozone forming ability, a better ozone reduction could be obtained if the emission reductions focused on the most potent ozone producers instead of reducing all VOC regardless of the species (McBride *et al.*, 1997).

In chemical environments where the production of ozone from an additional emission of VOC is larger than in any other chemical environment, an additional emission of NO_x will reduce the ozone. In those chemical environments where an emission of NO_x gives a large production of ozone, the ozone production from an additional VOC emission is very small.

The combined effect of an emission of both NO_x and VOC at the same time will not necessarily be equal to the sum of the individual contribution from each emission. The effect may be more than additive. In those cases where the ozone produced from an emission of VOC is very large, the additional ozone which is produced can thus not be cancelled out to a zero net effect by adding NO_x at the same time. The largest production of ozone from extra emissions of both NO_x and VOC at the same time is achieved in a highly polluted area with high background levels of both NO_x and VOC.

1.5   *Atmospheric chemistry of VOC*

Volatile organic compounds (VOC) are defined as all organic species which are emitted to the atmosphere in the gas phase. This is a rather loose definition (which has not been strictly scientifically established) but it has turned out to be practical and works in reality (SNV, 1990). In this context many different organic species fall within the group of VOC and they differ for example regarding volatility, water solubility, reactivity and atmospheric reaction path and hence their ability to produce ozone vary.

The most important reaction which VOC undergo in the atmosphere is reaction with a hydroxyl radical (OH) to form a peroxy radical (RO_2). When the peroxy radicals react with NO to form NO_2, the ozone concentration is directly affected as mentioned previously in Chapter 1.3.

The production of ozone caused by a certain VOC depends on the chemical and meteorological conditions of the environment into which the VOC is emitted. The availability of NO_x and VOC in the background is especially important since this controls whether the environment is in the low or the high NO_x regime.

Many VOC undergo rather similar reactions in the atmosphere but each individual species has its own reaction path. VOC which during their degradation produce many radicals will speed up the oxidation of all other VOC present and thus increase the ozone produced from them. Other VOC will form products with NO_x during their degradation and the overall ozone production from other VOC may then decrease in a low NO_x environment, where the availability of NO_x limits the ozone formation. The very same VOC may give a high ozone production under conditions with higher NO_x concentrations, where the availability of NO_x is not critical (Carter, 1994; Bowman and Seinfeld, 1994ab).

1.6   Ranking VOC according to their ability to produce ozone

As outlined above, there is a need for a tool to compare the ability to produce ground level ozone between different VOC. Several different concepts for VOC ranking have been suggested and most of them include the use of atmospheric models. Atmospheric photochemical models describe the chemical and meteorological features of the atmosphere and are used to study atmospheric processes.

There is a difference in approach in the VOC ranking employed in the US and in Europe. In the US, modelling studies to rank VOC are only performed for situations with very high ozone peak values under highly polluted conditions. In Europe, the ozone production in less polluted areas is also considered as well as integrated contributions to the ozone concentrations. The most commonly used methods are *Photochemical Ozone Creation Potentials* (POCP values) in Europe (Hough and Derwent, 1987; Derwent and Jenkin, 1991; Andersson-Sköld *et al.*, 1992; Simpson, 1995; Derwent *et al.*, 1996; Derwent *et al.*, 1998) and *Incremental Reactivities* (IR values) in the US (Carter and Atkinson, 1987; Carter *et al.*, 1995).

When atmospheric models are used to determine the ozone production from a certain VOC emission, two separate simulations are run, one with and one without an extra emission of that VOC. The amount of ozone which is produced through the additional emission of VOC is then calculated as the difference in ozone concentration between the two scenarios, divided by the amount of extra VOC added.

The POCP values are generally presented as relative values where the amount of ozone produced from a certain VOC is divided with the amount of ozone produced from an equally large emission of ethene (equation 4) (Derwent *et al.*, 1996).

$$\text{POCP}_i \;=\; 100 \;\times\; \frac{\text{ozone increment with the } i\text{th VOC}}{\text{ozone increment with ethene}} \qquad (4)$$

The POCP values can be based on the maximum difference in ozone concentration or on the average production of ozone over some time following the extra emission of VOC.

IR values are calculated based upon the ozone formation at the maximum ozone concentration occurring a few hours after the extra emission of VOC (Carter and Atkinson, 1989). Fast reacting species are therefore ranked much higher than slow reacting species for which a few hours is not enough time for the ozone production to take place. The Maximum Incremental Reactivity (MIR), which is often used, is calculated according to the same principle but with a NO_x concentration that will give the maximum production of ozone from the addition of an extra VOC emission.

One simple way to compare different VOC is to look at their rate constants for reaction with the hydroxyl radical, k_{OH}. These data are determined experimentally from smog chambers. They give an indication of how fast the VOC will react in the atmosphere but it only shows the very first step of the reaction pathway. Even though this rate is of great importance, since it opens up the VOC for further reactions in the atmosphere, it does not solely determine the amount of ozone being produced from a certain VOC (Japar *et al.*, 1991; Dimitriades, 1996).

Some VOC, e.g. alcohols, are soluble in water and will to some extent be washed out from the atmosphere through rain, and will thus be stopped from complete atmospheric degradation. A further development of the POCP concept in the future should account for water solubility and the possibility of washout.

1.7 Aim

The best way to determine the ozone production from a VOC emission through computer modelling, would be to perform individual atmospheric modelling studies whenever the effect of an emission is to be estimated at a certain location. This is however very time and cost consuming. It is therefore desired to work out a generally applicable concept, which can be used to estimate the effects from different emissions in various environments for most purposes. General concepts will however not be able to fully replace site specific model simulations. Site specific evaluation will still be needed as a complement in those cases when a detailed assessment or when quantifications of the increase in ozone load is required.

The aim of this project is to find a general way to present POCP values for different VOC under European conditions and to calculate such values for a large number of VOC. In order to do this, the robustness of the calculated POCP values has been analysed towards changes in various model parameters. The VOC/NO_x environment, which is known to be a crucial parameter that highly affects the POCP values, has been given special attention.

2 Methods for the critical analysis of the POCP concept

The POCP concept has been investigated and POCP values have been calculated for 83 different VOC, using the IVL photochemical trajectory model.

The POCP values have been calculated as the difference in ozone production between two separate simulations, one with and one without an extra emission (a point source) of a certain VOC.

2.1 The IVL photochemical trajectory model

The IVL model is a two-level model which describes the chemical development in an air mass following a trajectory in the atmospheric boundary layer. The model, which has been revised at IVL to fit Swedish conditions (Pleijel *et al.*, 1992; Andersson-Sköld *et al.*, 1992), was originally developed from the Harwell model (Derwent and Hov, 1979; Derwent and Hough, 1988) . Today, the IVL model explicitly describes the atmospheric fate of around 80 VOC and includes in total more than 800 chemical species participating in around 2000 chemical and photochemical reactions (Andersson-Sköld, 1995). The model is one of the most chemically detailed photochemical models in Europe and has been used in many comparison studies, most recently in the EUROTRAC model intercomparison study (Kuhn *et al.*, 1998). A detailed description of the model and of the model set-up is given in Altenstedt and Pleijel (1998).

2.2 Model set-up and parameters which have been tested within the study

The POCP values given in this report have been calculated using the IVL chemical scheme (Andersson-Sköld, 1995). For the critical analysis of the POCP concept however, most of the simulations have been performed using the less detailed chemistry from the EMEP model given in Simpson *et al.* (1993). The EMEP chemical scheme is also an explicit scheme but with much fewer species, in total 70 species taking part in 136 chemical and photo-chemical reactions. It has been compared to the IVL model in several comparison studies and the results from the two chemical schemes have shown to correlate well (Kuhn *et al.*, 1998; Pleijel *et al.*, 1996; Andersson-Sköld and Simpson, 1997).

In the detailed investigation of the POCP concept we have concentrated on only three different VOC to analyse the effect from varying different model parameters. The three species which have been studied are ethene, n-butane and o-xylene. They have been chosen because of their different abilities to produce ozone and because they are represented in both the IVL and the EMEP chemical schemes.

The model is defined by a large number of parameters which describe the chemistry and the meteorology of the atmosphere. The model parameters which have been studied to asses their importance for the calculation of POCP values are listed below:

- Initial concentrations of O_3, CO and CH_4
  The effect of giving NO_x and VOC initial concentrations was also tested.
- Background emissions of SO_2, CO, CH_4 and isoprene
- The shape of the point source emission (emission density · time of point source)
- Hour of the day for the point source emission
- The emission density of the VOC point source
  The absolute amount of species emitted in the point source was hereby varied.
- The distribution of the background VOC emissions
- Dry deposition velocities of O_3, HNO_3, NO_2, H_2O_2, SO_2, PAN and PAN analogues, aldehydes and organic peroxides.
- Meteorological parameters:
  Date
  Latitude
  Mixing height
  Temperature
  Relative humidity
  Cloudiness
- VOC/NO_x background emissions
  The absolute emissions of both NO_x and VOC as well as the VOC/NO_x ratio was varied.
  Further investigations were made through simulations where the emissions varied along the trajectories.
  Trajectories with varying emissions but the total integrated emissions kept constant were also studied.

The background emissions of NO_x and VOC have been given special attention since the availability of NO_x and VOC is critical for the ozone production. A total of 36 different scenarios have been simulated to cover a realistic range of VOC/NO_x emission scenarios within Europe.

The word scenario refers to the total model set-up used in a certain simulation. If the only parameters which vary between different simulations are the background emission of VOC and NO_x, these scenarios are also referred to as different chemical environments throughout the report.

2.3 Different ways to quantify the ozone formation

2.3.1 Different time scales

The production of ozone from an emission of VOC takes place on different time scales depending on how fast and by which reaction path the VOC react in the troposphere. Because of this, the POCP value of a specific VOC can vary significantly depending on how and when the formation of ozone is quantified. For a fast reacting VOC, the production of ozone reaches a narrow maximum shortly after the emission,

while for a slower reacting species, a broader maximum is obtained maybe not until a day or two after the emission. While the total amount of ozone produced from the fast and the slow reacting VOC may be fairly the same, there is still a large difference in the maximum contribution to the ozone concentration. Figure 2.1 shows an example of this by comparing the ozone production from ethene, n-butane and o-xylene.
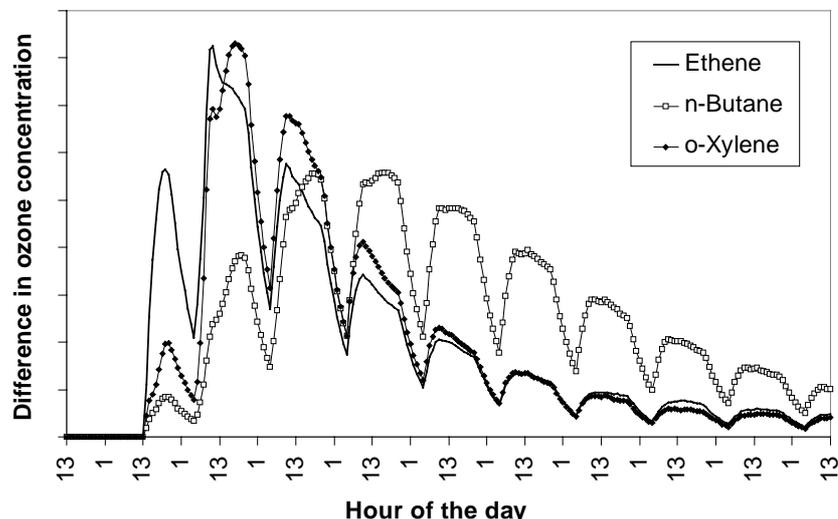
Figure 2.1   The ozone produced from a point source of ethene, n-butane and o-xylene.

Ozone is removed from the atmosphere through deposition. The amount of ozone which is deposited is proportional to the ozone concentration. The production of ozone from a point source emission of VOC will thus also give rise to a larger ozone deposition. The ozone which is deposited to the ground causes damage and should therefore also be considered in the evaluation of the ozone produced from an emission of a VOC.

For the investigation of the robustness of the POCP concept, the average ozone formation integrated over a time period of 96 hours after the emission of the point source has been used. This average ozone formation has also included the extra amount of ozone which has been deposited due to the point source of VOC, during the 96 hours after the emission (Altenstedt and Pleijel, 1998). The deposited ozone is expressed as a concentration in the results. It is calculated as the extra contribution to the ozone concentration which it would have given if it had not been removed through deposition.

Sunlight is needed for the production of ground level ozone but other meteorological parameters also affect the process. The optimal meteorological situation for ozone production is a day around mid summer with a high pressure, clear sky and low wind speed. These meteorological conditions are also favourable for accumulation of pollution in an air mass. Accumulation will normally not stay undisturbed in an air mass for longer than 4 consecutive days (Smith and Hunt, 1978). In a real life scenario, diffusion will dilute the effect of a point source when the trajectory moves further away from the emission source. In these model simulations, no horizontal diffusion has been considered and thus the modelled trajectories will become less realistic after a long period of simulation. Model simulations of POCP values should thus be limited in time. We have chosen to only consider the 96 hours following the

point source when we calculate the average ozone production since this is how long a meteorological situation which favours accumulation is sustained.

The maximum contribution to the ozone concentration from an emission of VOC has also been studied. Very high concentrations of ozone are considered harmful even if they are only sustained for a shorter period of time. When the maximum contributions to the ozone concentration have been calculated, the contributions to the deposited ozone has not been considered.

2.3.2 Relative and absolute POCP values

In many applications, a relative measure of the ozone production is adequate to make decisions regarding VOC control measures. However in some cases there is a need to quantify the absolute ozone production from a certain VOC. One example of this is in Life Cycle Assessments (LCA) where the production of ozone is to be compared with other environmental impacts. Relative values are generally more stable than the absolute values since many of the effects caused by a certain parameter cancel out as two identical model scenarios are compared with each other. This study has focused on the relative POCP values but the impact on the absolute ozone production is also discussed .

The relative POCP values have in this study been calculated as the ozone produced from each VOC divided by the ozone produced from the same point source of ethene. The POCP value for ethene has been set to 100.

3 Results from the critical analysis of the POCP concept

In the following chapter the highlights from the results of the critical analysis of the POCP concept will be presented. A more detailed description of the results is given in Altenstedt and Pleijel (1998).

For all the different model parameters that have been tested, the effects from adding a point source of ethene, n-butane or o-xylene have been studied. Both the absolute formation of ozone and the relative amount of ozone produced from each VOC compared with ethene have been studied.

3.1 Model parameters with a minor influence on the relative POCP values

For many of the parameters there are large variations in the absolute amount of ozone produced, while the relative ozone formation shows much less variation for each individual VOC. This is demonstrated in Figure 3.2 for variations in the dry deposition velocity of ozone. The dry deposition velocity has been varied in between a factor 0 and 2 times the default value. Figure 3.2a shows the average ozone production caused by a point source of ethene, n-butane or o-xylene. There is a large difference between the two cases having the lowest and the highest ozone dry deposition velocity for each individual VOC. The relative POCP values which are shown in Figure 3.2b however do not show this variation, but are rather stable. The POCP values of ethene are shown as a straight line since these values are calculated relative to themselves.
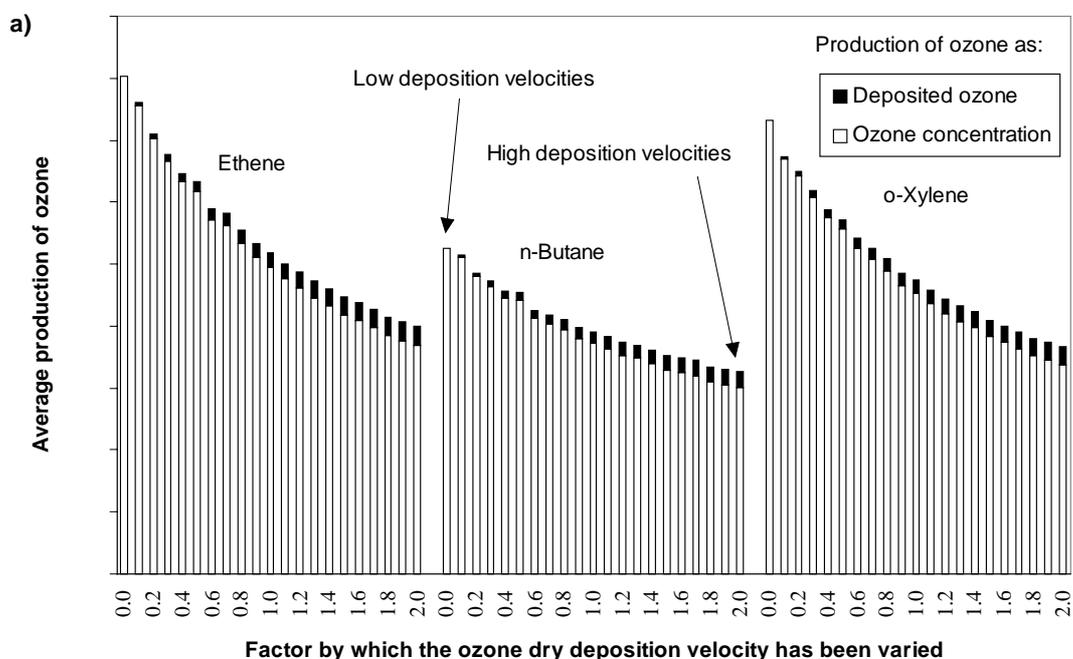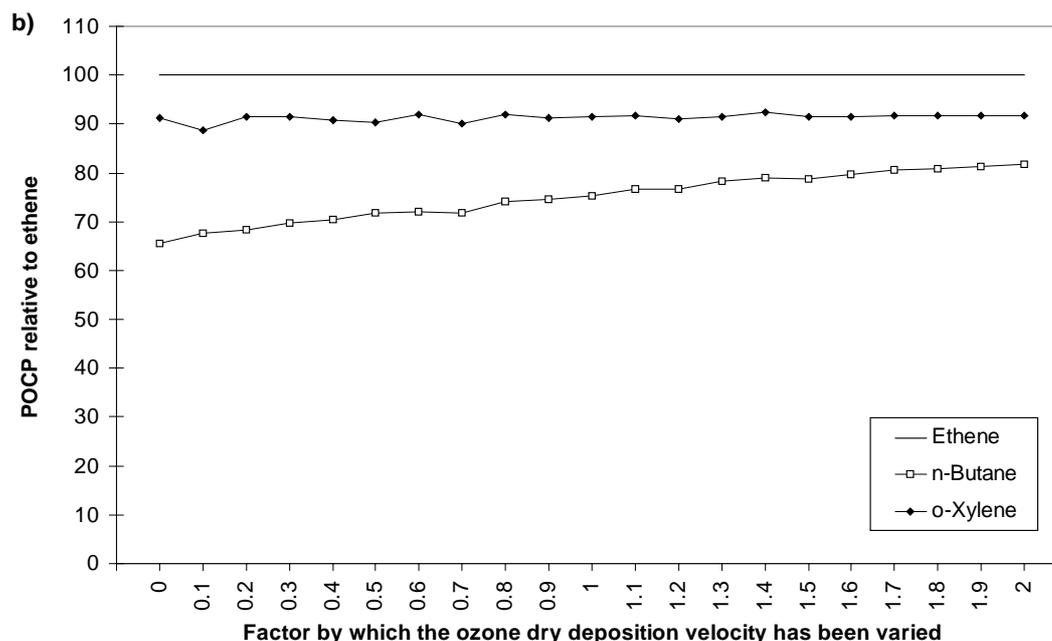
Figure 3.2   The *a) absolute* and *b) relative* average ozone production* caused by a point source of ethene, n-butane and o-xylene, in simulations with varying dry deposition velocity for ozone. The ozone deposition velocities increase from left to right, indicated for n-butane in a). The numbers on the x-axes gives the factors by which the default ozone dry deposition velocity has been varied in the different scenarios. * *Chapter 2.3.1 gives an explanation of how the average production of ozone is calculated.*

The parallel lines in Figure 3.2b show that the POCP for n-butane and o-xylene relative to ethene is not altered by changes in the ozone deposition velocity. It can thus be concluded that the dry deposition velocity of ozone is not critical for the calculation of relative POCP values. Most of the studied model parameters show the same behaviour as in Figure 3.2 above. Of the model parameters which have been studied, the background VOC and NO_x emissions and the hour of the day for the point source emission have turned out to be the most critical for the calculation of POCP values. The results for these parameters are discussed in more detail below.

3.2   *Background emissions of VOC and NO_x*

The production of ozone varies depending on the chemical environment, defined by the availability of NO_x and VOC in the background. The amount of ozone produced from a point source of VOC is larger in scenarios with high background NO_x emissions. Within each level of NO_x emissions, the production of ozone caused by a point source of VOC is larger in those scenarios where the background emissions of VOC are low, i.e. scenarios with a high VOC/NO_x ratio. This variation in the amount of ozone formed from a point source is observed for all three of the tested VOC. The relative POCP values however show a large variation between different chemical environments. The POCP values are more stable in the more polluted scenarios and it is also in these scenarios that most ozone is being produced from an individual point source. The scenarios which give the most divergent POCP values are those which experience the highest ratios of VOC to NO_x emissions.

Scenarios with varying emissions of NO_x and VOC have been run to see whether it would be possible to calculate the POCP values in a scenario starting in one chemical environment and ending in another, based on the known POCP values in two constant chemical environments. In this way, POCP values in a chemical environment which has not been studied, could be interpolated from a set of POCP values in different chemical reference environments.

The results from this investigation show that it is not possible to determine the ozone production from a point source of VOC in a certain chemical environment by interpolating the results from other known chemical environments. In scenarios which start in an environment limited by the availability of NO_x and proceed into another limited by VOC, the production of ozone is larger than in any of the constant scenarios. The trajectory which pass through both chemical environments is supplied with both NO_x and VOC and is thus not as strongly limited by any of the precursors as the initial single chemical environment trajectories.

The time of day for the change in chemical environment is also shown to be important since the change from VOC to NO_x sensitivity behaves differently depending on whether daytime or night-time chemistry rules.

3.3   Hour of the day for the VOC point source

The ozone produced from a point source of VOC, depends on at what hour of the day the point source is emitted. There is a clear diurnal variation with more ozone being produced from an emission source during the night or in the early morning and less
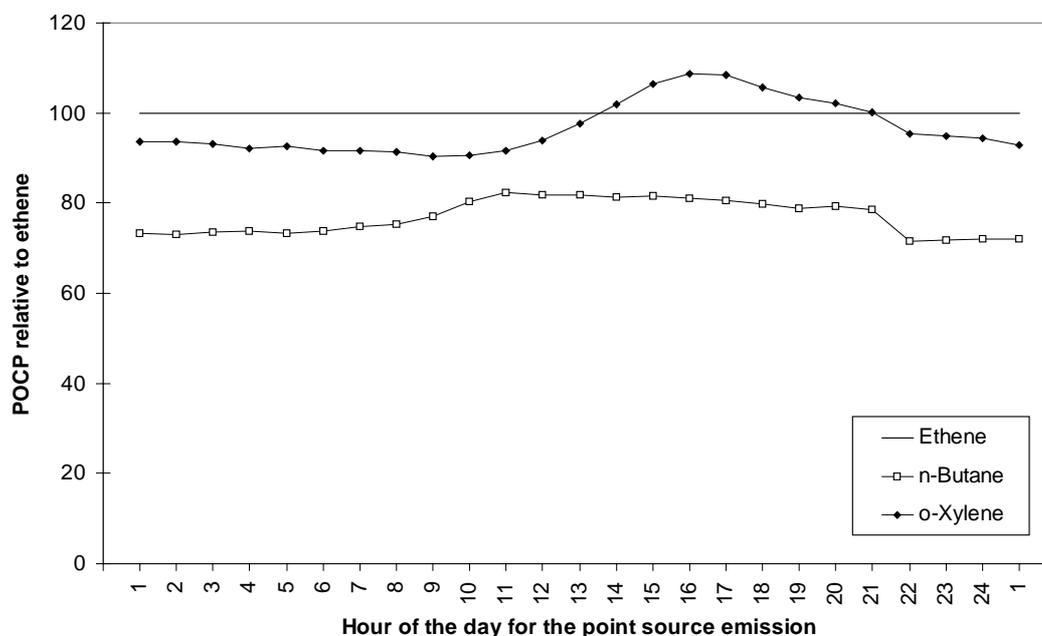
Figure 3.3   The relative average production of ozone* from a point source of ethene, n-butane and o-xylene in simulations with varying hour of the day for the point source emission. * *Chapter 2.3.1 gives an explanation of how the average production of ozone is calculated.*

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ozone being produced from the same source in the late afternoon. This diurnal variation does not show exactly the same pattern for different VOC. The result is a change in the ordering of POCP values between ethene and o-xylene for a point source emitted during the afternoon. Apart from this change in ordering between ethene and o-xylene, the relative POCP values are rather stable (Figure 3.3).

Several reasons for these changes in POCP values, due to the hour of the day for the point source emission, have been suggested and investigated within the study. Many theories have been ruled out and the explanation is thought to lie in the difference in atmospheric chemical reaction path between ethene and o-xylene. The observed change of ordering in POCP values has however not been fully explained and further studies are therefore necessary.

In the final calculation of POCP values we have chosen to only consider a point source emitted at one specific hour of the day despite the fact that the critical analysis shows a large variation in POCP values, depending on the hour of the day for the point source (Figure 3.3). The background emissions of NO_x and VOC have a very large impact on the POCP values and variations in these parameters have therefore been considered in the calculation of POCP values through the use of five scenarios with different background emissions of NO_x and VOC. The critical analysis showed larger variations in POCP values depending on the background emissions of NO_x and VOC than depending on the hour of the day for the point source.

The five chemical environments produce ranges of POCP values which cover the variations caused by the different levels of background emission of NO_x and VOC, tested in the critical analysis.

This provides no absolute guarantee that the variation in POCP values depending on the hour of the day for the point source is always fully covered by the ranges in POCP values produced by the five different chemical environments, for all possible VOC in all environments. The results from the critical analysis are however an indication that the hour of the day need not be considered if the calculation of POCP ranges are based on the five chosen chemical environments.

Please note that the variation in POCP value for o-xylene in Figure 3.3 is not reflected by the POCP range for o-xylene in the final calculation of POCP ranges in Chapter 6. This is because the results in Figure 3.3 are calculated using the EMEP chemical scheme while the final POCP ranges, presented in Chapter 6, are calculated using the IVL chemical scheme. The two chemical schemes are discussed in Chapter 2.2.

4   Conclusions from the critical analysis of the POCP concept

The method of using POCP values as a ranking system between different VOC, has been critically evaluated in this study. It can be concluded that the POCP concept is a useful tool to rank different VOC. As shown in this study, the ranking may change as some of the model parameters are changed. The POCP value for each individual VOC stays within a certain range, which justifies the use of a ranking system instead of treating all VOC as a homogeneous group. VOC emission reductions can be made more efficient for ozone control if the more potent ozone producers are reduced compared to an overall reduction of VOC. This fact is emphasised also by the results from other authors (Leggett, 1996; Derwent *et al.*, 1998). The calculation of POCP values for 83 different VOC in different chemical environments, which are given in Chapter 6, confirm this conclusion.

5 Selecting model set-up for calculation of POCP

Based on the results from the critical analysis of the different model parameters, the modelling conditions used for the calculation of POCP values have been determined. Relative values are generally more stable than the absolute values since many of the effects caused by a certain parameter cancel out as two identical model scenarios are compared with each other.

The production of PAN follows the production of ozone to a large extent. The chemical reaction path differs from one VOC to another so the production of PAN will vary between species. The ranking of individual VOC would therefore change if the production of PAN was considered instead of the ozone formation.

The decisions which have been made regarding different model parameters and how they should be considered in POCP calculations, using the IVL model, are listed below. The parameters are set so that emissions and other geographical parameters should reflect average European conditions while more non site specific meteorological parameters are chosen to give a maximum production of ozone.

5.1 Initial concentrations

Initial concentrations are only given for ozone, CO and CH_4. The initial concentrations are chosen to represent average European concentrations and the values are set to 70 ppb for ozone, 200 ppb for CO and 1700 ppb for CH_4.

5.2 Background emissions of SO_2, CO, CH_4 and isoprene

The background emissions of SO_2 and CH_4 are set to 6 and 10 tonnes·km^{-2}·$year^{-1}$ which are average European emissions based on CorinAir 90 (EEA, 1995). The isoprene emissions are set to 0.26 tonnes·km^{-2}·$year^{-1}$, reflecting average European emissions during the growing season (Simpson *et al.*, 1995). The emissions of CO are varied along with the VOC emissions with a CO/VOC ratio of 3.6 which reflect average European conditions.

5.3 The shape of the point source emission

The point source emission is emitted during 60 s since this reflects a reasonable time for an air mass to pass over an industrial plant or other area with specific emissions.

5.4 Hour of the day for the VOC point source

There is a clear diurnal variation in the amount of ozone produced from a point source depending on the hour of the day for the emission lasting for 60 s. The critical analysis shows that the explanation to the observed pattern must lie within the atmospheric

chemistry but no individual reactions have yet been identified as being responsible for the phenomena.

A point source early in the morning gives a higher ozone production than an emission at any other time of the day. Industrial activity and traffic is however not as active this early in the morning and the point source is therefore emitted at 8 a.m. when calculating POCP values. This is compatible with the decision that non site specific meteorological parameters are chosen to give a maximum production of ozone.

5.5 *The emission density of the VOC point source*

The emission density of the point source is set to 360 tonnes$\cdot$km$^{-2}\cdot$year^{-1}, which is high enough to avoid the noise level and numerical errors associated with it. It is desirable to keep down the size of the point source in order to avoid unnecessary disturbance of the chemical environment into which it is emitted. If a very large point source is released, this will alter the chemical environment and the results will not be representative for the intended original environment.

5.6 *The distribution of the background VOC emissions*

The background VOC is distributed as average Swedish VOC emissions.

5.7 *Dry deposition velocities*

The default deposition velocities which are used in the IVL model are used to calculate POCP values.

5.8 *Meteorological parameters*

The date is set to the 21st of June which is the longest day of the year and the cloudiness is set to zero. This maximises the photochemical activity in the simulations.

The mixing height of the boundary layer is set to 150 m during the night and then increases up to 1000 m during the morning and mid day hours. The temperature is set to around 25ºC and the relative humidity to around 60 % as average values over the day and both these parameters have a diurnal variation following the angle of the sun. The values of these parameters describe realistic meteorological conditions which are favourable for ozone production in Europe.

The latitude is set to 50ºN which corresponds to the central parts of Europe, e.g. the exact latitude for Frankfurt in Germany and Prague in the Czech Republic.

5.9 *Background emissions of VOC and NO$_x$*

The chemical environment defined by the availability of NO$_x$ and VOC has a large impact on the calculated POCP values. It affects both the absolute production of ozone and the relative contribution from individual VOC. It is therefore not adequate to calculate POCP values for one chemical environment, for general use in any chemical environment. On the other hand it is not practically possible to calculate POCP values for each single chemical environment. For certain applications it will always be necessary to make site specific calculations to be able to make a correct assessment of the photochemical ozone production.

Five different chemical environments are selected to get a representative range of POCP values under European conditions. The chemical environments are not chosen to represent typical average European emission scenarios even though all of the scenarios have emission densities and VOC/NO$_x$ ratios which are realistic and representative for Europe. The choice of scenarios is instead made to get the extremes in POCP values to make sure that all possible POCP values for any European emission scenario are within the resulting range in POCP values. POCP values are calculated for each of the chemical environments and indicate the range in ozone production ability for each individual VOC, under European conditions. The scenarios are selected to include both NO$_x$ and VOC limited scenarios.

The emission densities of NO$_x$ and VOC are kept constant during the trajectories. The simulations using varying emissions during the trajectories lead to very different results, especially if the changes in emissions cause a change in NO$_x$ to VOC sensitivity or the other way around. In the design of generally applicable POCP values, the use of scenarios with constant emissions is thus more useful.

The choice of the five chemical environments is justified below. The names of the environments, which are given in brackets, refer to the notation used in Altenstedt and Pleijel (1998), where a more detailed description of the critical analysis is given.

5.9.1 NO$_x$ limited scenario

In NO$_x$ limited scenarios, NO$_x$ control is more effective in reducing ozone than VOC control. The amount of ozone produced from a point source of NO$_x$ varies largely between different environments and is largest in NO$_x$ limited scenarios. The absolute production of ozone from a point source of VOC on the other hand is not more than a factor two or three times lower in NO$_x$ limited scenarios compared to the most VOC limited scenarios. The fact that NO$_x$ control is more efficient than VOC control in NO$_x$ limited scenarios is thus not because the effect on ozone from VOC control is reduced to a minimum, but can instead be explained by the increased effect from NO$_x$ control. It is thus desirable to rank different VOC according to their potential to form ozone also in NO$_x$ limited scenarios.

We include one NO$_x$ limited scenario to demonstrate the differences in POCP ranking which this may give, compared to more highly polluted scenarios. In Europe, a concentration of 40 ppb is presently used as a cut-off concentration above which

significant adverse affects on plants have shown to occur. In many low emission scenarios this limit is not exceeded, and emission sources which contribute to ozone formation mainly in these areas are therefore not as urgent to reduce. The low NO_x scenario A (N3v4) with background emissions of $NO_x = 0.3$ tonnes·km^{-2}·$year^{-1}$ and $VOC = 1$ tonnes·km^{-2}·$year^{-1}$ causes a total ozone concentration above 40 ppb and has therefore been chosen. The VOC emissions are set higher than the NO_x to give a strictly NO_x limited scenario. This emission density is representative for central to northern Scandinavia.

5.9.2 VOC limited scenarios

Scenario D (N6v6) and E (N6½v6) which have VOC emissions of 10 tonnes·km^{-2}·$year^{-1}$ and NO_x emissions of 10 or 20 tonnes·km^{-2}·$year^{-1}$ are chosen to represent highly polluted, VOC sensitive emission scenarios. Scenario D which have both NO_x and VOC emissions of 10 tonnes·km^{-2}·$year^{-1}$ reflects the highest emission densities in Europe on the 150 by 150 km EMEP grid square scale (e.g. Holland and Belgium). Scenario E with the NO_x emissions set to 20 tonnes·km^{-2}·$year^{-1}$ is however also included since this gives a strictly VOC limited scenario. The emission densities may locally be many times higher than the values based on a 150 km resolution, but the high emissions are not maintained as the air moves over the continent. Scenario E is included to indicate the effects from such high local emissions.

5.9.3 Intermediate scenarios

In between the NO_x and VOC limited scenarios, two additional scenarios are chosen. These are selected to represent realistic European scenarios which give some variations in POCP ranking to make sure that the scenarios cover the range of possible POCP values. The two additional scenarios which are chosen are B (N5v4) and C (N5v6) with $NO_x = 3$ tonnes·km^{-2}·$year^{-1}$ and $VOC = 1$ or 10 tonnes·km^{-2}·$year^{-1}$. Higher or lower VOC emissions than this are not compatible with the chosen NO_x emission density in order to represent realistic emission scenarios in Europe. The reason for not including scenario N5v5 instead of scenarios B and C is because this does not give such large variation in POCP values. The VOC/NO_x ratio of scenario N5v5 is the same as in scenario D, which is already included among the chosen scenarios, and these two scenarios show similar POCP values.

In Table 5.1 the five different chemical environments, which are chosen for calculation of POCP values, are defined.

Table 5.1   The emission densities of NO_x, VOC and CO in the five chemical environments selected for calculation of POCP values. The names within brackets refer to the notation used in Altenstedt and Pleijel (1998).

	NO_x	VOC	CO
Chemical environment	(tonnes$\cdot$km$^{-2}\cdot$year^{-1})		
A (N3v4)	0.3	1	3.6
B (N5v4)	3	1	3.6
C (N5v6)	3	10	36
D (N6v6)	10	10	36
E (N6½v6)	20	10	36

The selected scenarios are hypothetical and are not meant to describe real plumes of air passing over Europe. They are an attempt to describe the very complex situation in Europe with large variations in emissions and to estimate the effect that these variations in emissions may have on the POCP values.

6 POCP values under European conditions

6.1 The ozone production from VOC and NO_x in the troposphere

It would be very useful if NO_x could be ranked and be given a POCP value just like individual VOC. Simulations have been performed to check in a similar way as for the VOC, how the ozone production from a NO_x point source emission is affected by changes in the environment. Since the hour of the day for the point source and the VOC/NO_x environment turned out to be of importance for a VOC point source, these parameters have been investigated also for a NO_x point source. The simulations show that these parameters influence the amount of ozone produced from a NO_x point source to a very large extent.

The results from the simulations clearly indicate the difficulties associated with trying to assess the impact from NO_x in the same way as for VOC. NO_x and VOC react very differently in the atmosphere since NO_x works as a catalyst and is not consumed in the ozone production process, while VOC is consumed and can be regarded as the fuel in the process. Because of this, tropospheric ozone formation is a non linear process with two different states of the chemistry often referred to as high NO_x and low NO_x regimes. In the low NO_x regime, the atmosphere is very sensitive to NO_x while changing the VOC emissions has less impact. In this system there is not enough catalyst (NO_x) to make use of all the available fuel (VOC) for ozone production. In the high NO_x regime there is enough NO_x to make the ozone formation from VOC degradation very effective and the system is therefore more sensitive to changes in the VOC emissions. An additional emission of NO_x causes an initial temporary decrease in ozone in almost any chemical environment due to the fast reaction between NO and ozone. The titration is only temporary and in most cases an extra NO_x emission will cause a net increase in ozone relatively soon after the emission. In the high NO_x regime however, the addition of further NO_x will actually reduce the ozone concentration also after several days of simulation.

POCP values for VOC are calculated relative another VOC, generally ethene. Due to the non linearity of the tropospheric chemistry, the POCP values for NO_x can thus assume negative values for some conditions and may thereby be more confusing than helpful. It is therefore more useful to discuss NO_x versus VOC as a group of species regarding emission reductions and not as an individual species among other VOC.

The ozone production from NO_x and a mixture of different VOC have been tested in 25 different chemical environments including the five used for calculation of POCP values for individual VOC. The VOC mixture which was added in these tests had the same distribution of species as the VOC emitted from the background.

The 25 chemical environments all reflect realistic conditions for Europe. The emission densities for the scenarios are given in Table 6.1.

Table 6.1   The chemical environments in which the ozone production from a point source of NO_x and a point source of VOC have been tested. The five environments (A-E) were used for calculation of POCP values for individual VOC. (The names of the scenarios refer to the notation used in Altenstedt and Pleijel (1998) with the difference that the letter z was used where the symbol ½ is used below.)

Chemical environment		NO_x	VOC	CO
		(tonnes·km^{-2}·year^{-1})		
N3v4	(Environment A)	0.3	1	3.6
N4v4		1	1	3.6
N4v4½		1	2	7.2
N4v5		1	3	10.8
N4v5½		1	6	21.6
N4½v4		2	1	3.6
N4½v4½		2	2	7.2
N4½v5		2	3	10.8
N4½v5½		2	6	21.6
N5v4	(Environment B)	3	1	3.6
N5v4½		3	2	7.2
N5v5		3	3	10.8
N5v5½		3	6	21.6
N5v6	(Environment C)	3	10	36
N5½v4		6	1	3.6
N5½v4½		6	2	7.2
N5½v5		6	3	10.8
N5½v5½		6	6	21.6
N5½v6		6	10	36
N5½v6½		6	20	72
N6v5½		10	6	21.6
N6v6	(Environment D)	10	10	36
N6v6½		10	20	72
N6½v6	(Environment E)	20	10	36
N6½v6½		20	20	72

In Figure 6.1 the ozone production caused by a point source of NO_x or VOC respectively is shown along a trajectory in background scenario N5V5½.
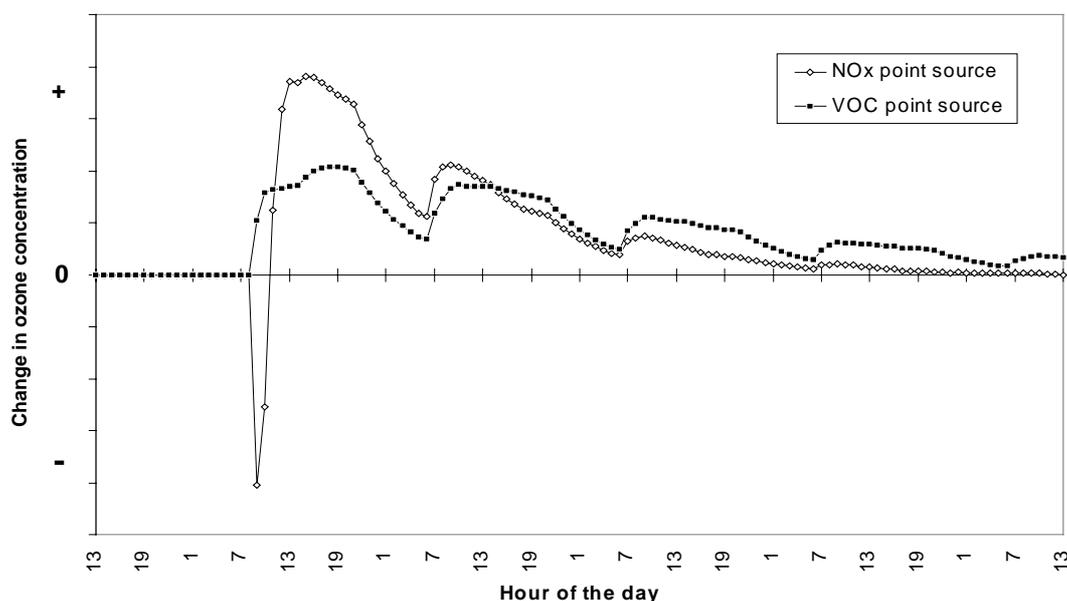
Figure 6.1   The principle of ozone production from a point source of NO_x or VOC in the environment N5V5½ which has background emissions of NO_x = 3 tonnes·km^{-2}·year^{-1} and VOC = 6 tonnes·km^{-2}·year^{-1}.

The point source of NO_x is emitted as 95 % NO and 5 % NO_2, the same distribution is used for the background NO_x emissions. There is an instant titration of the ozone concentration due to the fast reaction between NO and O_3 which produces NO_2. As the NO_2 is photolysed, the ozone production speeds up and the decrease in ozone changes into an increase (Figure 6.1). When instead an equally large source of VOC (by weight) is added, the change in ozone is positive and is maintained during a longer period of time. Note that Figure 6.1 only shows what happens in one specific environment. In a very low NO_x scenario the difference between the changes in ozone from NO_x and VOC will be much larger and in a very high NO_x environment the decrease in ozone will not change into an increase during the four days of simulation.

In Figure 6.2 the ozone production from a point source of NO_x or VOC is given for the 25 simulated scenarios. An equally large point source (by weight) has been added for both NO_x and VOC which makes it possible to compare the effect in different chemical environments. The background emission scenarios are sorted primarily by their NO_x emissions so that the scenarios with low NO_x background emissions are to the left and the scenarios with high NO_x background emissions are to the right on the x-axis. Within each level of NO_x emissions the scenarios are sorted by their VOC background emission with low VOC emission to the left and high VOC emissions to the right.

The absolute production of ozone from a point source emission varies depending on the chemical environment, defined by the availability of NO_x and VOC in the background. As can be seen in Figure 6.2, the average amount of ozone produced
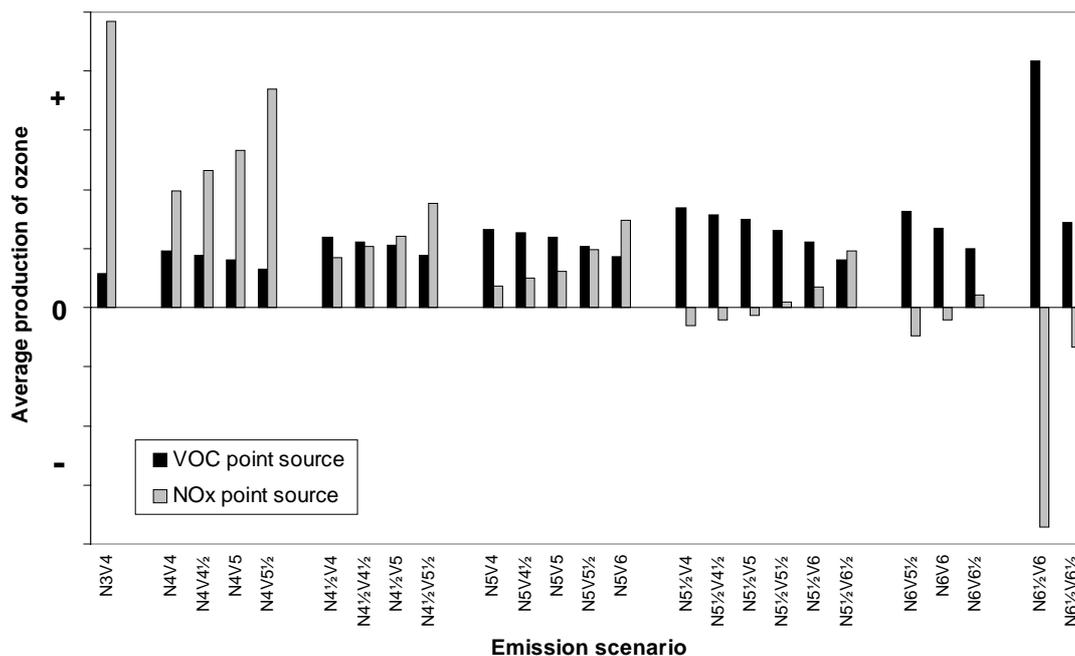
Figure 6.2   The average ozone production* from a point source of NO_x or VOC in different chemical environments according to Table 6.1. * *Chapter 2.3.1 gives an explanation of how the average production of ozone is calculated.*

from a point source of VOC is larger in scenarios with high background NO_x emissions. A point source of NO_x produces more ozone in the scenarios with low NO_x emissions in the background. Within each level of NO_x emissions, the production of ozone due to a point source of VOC is larger in the scenarios where the background emissions of VOC are low, i.e. the scenarios with a high VOC/NO_x ratio. The opposite is true for a NO_x point source which gives a larger increase in ozone for those scenarios with higher VOC background emissions for a fixed level of NO_x background emissions. For the scenarios with the highest NO_x background emissions, a point source of NO_x decreases the ozone concentration.

The response from an additional emission of NO_x varies much more than the response from a VOC emission (Figure 6.2). In environments with low NO_x emissions from the background, an extra emission of NO_x gives a large average production of ozone but in some high NO_x environments the average production of ozone can be negative, i.e. that the additional NO_x emission causes a net reduction of the ozone. In the low NO_x scenarios, where a NO_x point source causes the largest ozone formation, VOC emission reductions have generally not been considered important due to the much higher ozone reduction efficiency from NO_x emission reductions. The response from a VOC emission is however only around a factor two or three lower than the response in the majority of the scenarios, which is clearly seen in Figure 6.2.

Many other oxidants are formed in the troposphere along with ozone. The most important of these are peroxyacetyl nitrate (PAN) and its analogues. The concentrations of PANs are so far not high enough to constitute a threat to human health in Europe, but these species are of importance since they act as temporary sinks for NO_2. They are formed from the reaction between NO_2 and peroxy acetyl radicals, but since they are temperature sensitive they can decompose and thus release NO_2

back to the troposphere again. In Figure 6.3 the average production of PANs is given in the same way as for ozone (Figure 6.2).
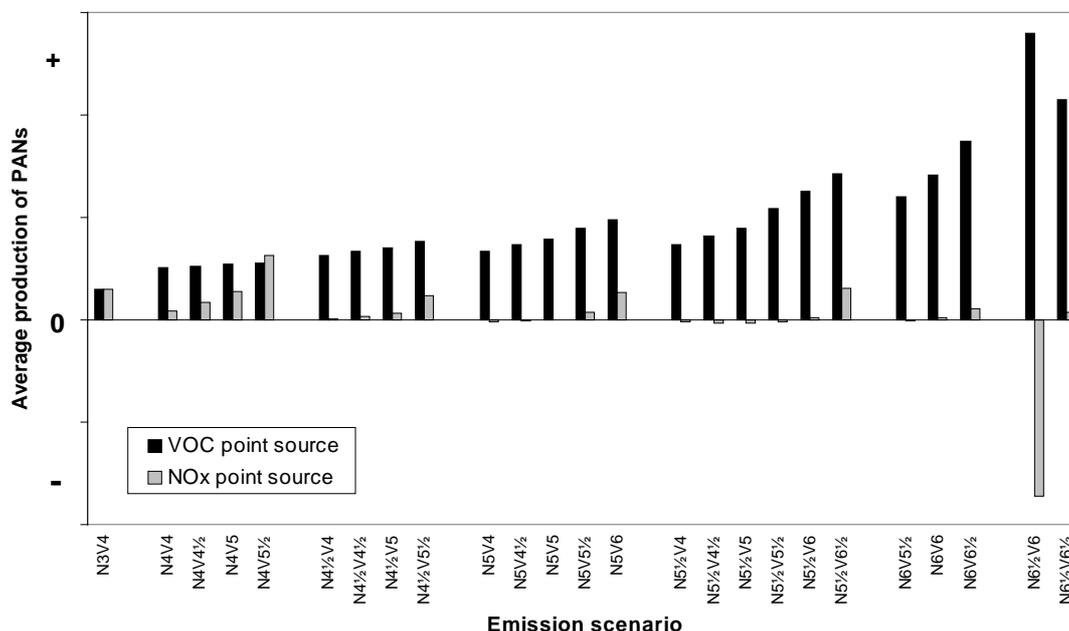
Figure 6.3   The average production of PANs* from a point source of NO$_x$ or VOC in different chemical environments according to Table 6.1. * *The average production of PANs is calculated in the same way as for ozone. The principle for how this is done is explained in Chapter 2.3.1.*

The average production of PANs from a point source of NO$_x$ or VOC in different environments does not behave in the same way as the average production of ozone. The formation of PANs caused by an emission of VOC is almost in every environment larger than the production of PANs from an emission of NO$_x$. The production of PANs from an emission of VOC is much larger in the high NO$_x$ scenarios than in the low NO$_x$ scenarios. A point source of NO$_x$ causes a reduction in PANs for one high NO$_x$ environment. This is the same environment where the largest average production of PANs is obtained for a point source of VOC (scenario N6½V6). Scenario N6½V6 also gives the largest reduction in ozone from an emission of NO$_x$ and the largest average production of ozone from an emission of VOC (Figure 6.2).

The *maximum* changes in ozone and PANs concentrations have also been studied just like the *average* productions of ozone and PANs, caused by a point source of NO$_x$ or VOC. For both ozone and PANs, the maximum changes are naturally larger than the average changes and none of the environments shows a negative maximum change. The relation between the ozone production from an emission of VOC or NO$_x$ is not very different when maximum changes are considered instead of average changes. If the maximum changes in ozone are studied, the differences in response between an additional emission of NO$_x$ or VOC are however more pronounced . The maximum and average changes in PANs do not show the same overall pattern between different environments. The overall pattern of the maximum changes in PANs is instead quite similar to that of the maximum changes in ozone.

In Figure 6.4 the production of ozone caused by a NO$_x$ point source in the 25 different environments are shown as the largest negative change, the average production and the maximum change in ozone to see how these parameters vary.
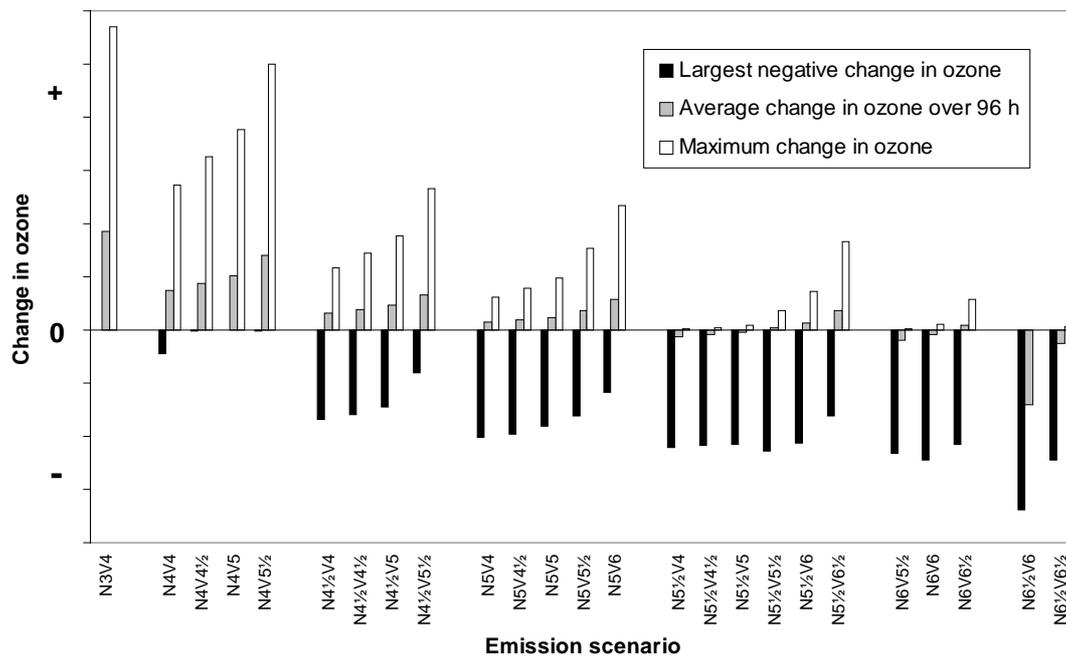
Figure 6.4　　The production of ozone caused by a point source of NO$_x$ in different chemical environments according to Table 6.1. The effect on the ozone is given in three different ways, as the largest negative change in ozone concentration, as the average production of ozone* and as the maximum change in ozone concentration.　　*
Chapter 2.3.1 gives an explanation of how the average production of ozone is calculated.

For the scenarios where the average production of ozone caused by a point source of NO$_x$ is positive, the average changes are in between 20 and 35 % of the maximum changes in ozone concentration due to the same point source of NO$_x$. There is also a relation between the largest negative changes and the maximum changes in ozone concentration. The larger the initial reduction in ozone due to the titration with NO, the smaller the maximum change in ozone from the same point source of NO$_x$. This is clearly seen at the NO$_x$ emission levels N4½, N5 and N5½ in Figure 6.4.

6.2　Should VOC or NO$_x$ emissions be reduced in order to fight ozone?

In many real life situations the choice stands between reducing the emissions of VOC or NO$_x$. Since NO$_x$ and VOC react so differently in the atmosphere it is complicated to foresee the effects of emission reductions and thus to decide which reduction strategy to use.

The results from adding a point source of either NO$_x$ or VOC in 25 different environments give a general overview on the relative importance of NO$_x$ and VOC for the ozone formation. It should be noted that the graphs show the effect of equally large point sources, while in a real life situation different amounts of NO$_x$ and VOC

might be compared. It is also important to remember that the combined effect from a concurrent emission or emission reduction of both NO_x and VOC is not equal to the sum of the individual emissions or emission reductions.

Additional NO emissions will always reduce the ozone concentration in the close vicinity of the emission source. Additional emissions of NO_x may even in a regional perspective reduce the ozone concentration in high NO_x environments. This means that if the NO_x emissions are reduced in a high NO_x environment, e.g. the Milan area, this will actually increase the ozone concentration. In order to fight high ozone concentrations, the solution is not to emit huge quantities of NO_x because this will lead to ozone production further away from the emission sources and also increase the NO_2 concentrations near the emission sources. A high NO_2 concentration is a threat to human health and may also contribute to acidification. The potential increase in ozone concentration, caused by NO_x emission reductions in high NO_x environments, may be overcome by concurrent reductions of VOC emissions.

It is easier to assess the effect on the ozone production from a VOC emission than the effect from a NO_x emission, since the addition of VOC in almost all cases will result in an increased ozone concentration. The picture is much more complicated for NO_x, as explained in Chapter 6.1. This was clearly demonstrated in Figure 6.4 where the negative, average and maximum changes in ozone from a point source of NO_x were given. An emission of NO_x will cause a different production of ozone not only depending on the chemical environment but also depending on whether average or maximum changes in concentrations are studied in that environment. Depending on the local environmental focus in the area of the emission in question, the maximum change in ozone may be considered much more harmful than an average increase in ozone over a longer period of time. The effect of a NO_x emission may thus need to be quantified in different ways in order to decide whether an emission reduction strategy is efficient and environmentally sound or not.

The chemistry of the tropospheric ozone formation has been the subject of research for over a hundred years and still the question of NO_x versus VOC control is not fully solved. There is so far no simple equation to decide whether the best strategy to fight ozone is to reduce NO_x or VOC in a certain environment by just looking at the meteorology and the chemistry of that environment. In some emission scenarios it may be obvious which emission reductions to perform but this is rather the exception than the rule. To be able to make an environmentally correct assessment of whether to reduce NO_x or VOC emissions in individual cases, there is thus generally no other way to achieve this than to perform more detailed model simulations adjusted to the local conditions.

6.3   POCP values for individual VOC

POCP values have been calculated for 83 different VOC which are given in Table 6.2. All POCP values are expressed as relative values using the ozone formation from ethene as a reference (see equation 4 on page 5). Ethene is given the POCP value 100.

Table 6.2　83 different VOC for which European POCP ranges have been calculated. The chemical structure and the molecular weights are given to facilitate identification.

VOC name	Chemical structure	M (g/mole)
Alkanes		
methane	CH_4	16
ethane	C_2H_6	30
propane	C_3H_8	44
butane	C_4H_{10}	58
i-butane	$CH_3CH(CH_3)CH_3$	58
pentane	C_5H_{12}	72
i-pentane	$CH_3CH(CH_3)C_2H_5$	72
hexane	C_6H_{14}	86
2-methylpentane	$CH_3CH(CH_3)C_3H_7$	86
3-methylpentane	$C_2H_5CH(CH_3)C_2H_5$	86
heptane	C_7H_{16}	100
octane	C_8H_{18}	114
2-methylheptane	$CH_3CH(CH_3)C_5H_{11}$	114
nonane	C_9H_{20}	128
2-methyloctane	$CH_3CH(CH_3)C_6H_{13}$	128
decane	$C_{10}H_{22}$	142
2-methylnonane	$CH_3CH(CH_3)C_7H_{15}$	142
undecane	$C_{11}H_{24}$	156
2-methyldecane	$CH_3CH(CH_3)C_8H_{17}$	156
dodecane	$C_{12}H_{26}$	170
methylcyclohexane	$(CH_3)cykloC_6H_{11}$	98
Alkenes		
ethene	$CH_2=CH_2$	28
propene	$CH_2=CHCH_3$	42
1-butene	$CH_2=CHC_2H_5$	56
2-butene	$CH_3CH=CHCH_3$	56
i-butene	$CH_2=C(CH_3)CH_3$	56
1-pentene	$CH_2=CHC_3H_7$	70
2-pentene	$CH_3CH=CHC_2H_5$	70
2-methyl-1-butene	$CH_2=C(CH_3)C_2H_5$	70
2-methyl-2-butene	$CH_3C(CH_3)=C_2H_5$	70
isoprene	$CH_2=C(CH_3)CH=CH_3$	68
styrene	$C_6H_5CH=CH_2$	104
Alkynes		
acetylene (ethyne)	$CH{\equiv}CH$	26
Aromatics		
benzene	C_6H_6	78
toluene	$(CH_3)C_6H_5$	92
o-xylene	$o\text{-}(CH_3)_2C_6H_4$	106
m-xylene	$m\text{-}(CH_3)_2C_6H_4$	106
p-xylene	$p\text{-}(CH_3)_2C_6H_4$	106
ethylbenzene	$(C_2H_5)C_5H_5$	106
1,2,3-trimethylbenzene	$1,2,3\text{-}(CH_3)_3C_6H_3$	120
1,2,4-trimethylbenzene	$1,2,4\text{-}(CH_3)_3C_6H3$	120
1,3,5-trimethylbenzene	$1,3,5\text{-}(CH_3)_3C_6H3$	120

Continuation of **Table 6.2**

m-ethyltoluene	m-$(CH_3)(C_2H_5)C_6H_4$	120
p-ethyltoluene	p-$(CH_3)(C_2H_5)C_6H_4$	120
o-ethyltoluene	o-$(CH_3)(C_2H_5)C_6H_4$	120
n-propylbenzene	$(C_3H_7)C_6H_5$	120
i-propylbenzene	$(CH(CH_3)_2)C_6H_5$	120

Aldehydes		
formaldehyde (methanal)	$HCHO$	30
acetaldehyde (ethanal)	CH_3CHO	44
propionaldehyde (propanal)	C_2H_5CHO	58
butyraldehyde (butanal)	C_3H_7CHO	72
i-butyraldehyde (methylpropanal)	$CH(CH_3)_2CHO$	72
valeraldehyde (pentanal)	C_4H_9CHO	86
glyoxal	$CH(O)CHO$	58
methylglyoxal	$CH_3C(O)CHO$	72
acrolein	$CH_2=CHCHO$	56
methacrolein	$CH_2=C(CH_3)CHO$	70
benzaldehyde	C_6H_5CHO	106

Ketones		
acetone (propanone)	$CH_3C(O)CH_3$	58
ethyl-methyl-ketone (butanone)	$CH_3C(O)C_2H_5$	72
methyl-ibutyl-ketone	$CH_3C(O)CH_2CH(CH_3)CH_3$	100

Alcohols		
methanol	CH_3OH	32
ethanol	C_2H_5OH	46
i-propanol	$CH(CH_3)_2OH$	60
n-butanol	C_4H_9OH	74

Esters		
methylacetate	$CH_3C(O)OCH_3$	74
ethylacetate	$CH_3C(O)OC_2H_5$	88
n-butylacetate	$CH_3C(O)OC_4H_9$	116
s-butylacetate	$CH_3C(O)OCH(CH_3)C_2H_5$	116

Ethers and organic acids		
dimethylether	CH_3OCH_3	46
diethylether	$C_2H_5OC_2H_5$	74
methyl-tbutyl-ether	$CH_3OC(CH_3)_2CH_3$	88
acetic acid	$CH_3C(O)OH$	60

Chlorocarbons		
dichloromethane	CH_2Cl_2	84.9
1,1-dichloroethane	CH_3CHCl_2	98.9
1,2-dichloroethane	CH_2ClCH_2Cl	98.9
1,1,1-trichloroethane	CH_3CCl_3	133.3
trichloroethene	$CHCl=CCl_2$	131.3
tetrachloroethene	$CCl_2=CCl_2$	165.7

Others		
methyl mercaptan (methanethiol)	CH_3SH	44
dimethyl sulfide	CH_3SCH_3	58
dimethyl disulfide	$CH_3S_2CH_3$	86
carbon monoxide	CO	28

6.3.1 POCP ranges instead of site specific POCP values

POCP values have been calculated for individual VOC in five different chemical environments. The five scenarios have been selected in order to produce the extremes in POCP values representative for the varying conditions in Europe and not because they statistically represent the emissions in Europe. The scenarios include both low NO_x and high NO_x scenarios and have a variation in emission densities and VOC/NO_x ratios. The results from the calculations in the five chemical environments gives a span of POCP values for each VOC under European conditions.

The reason for choosing those scenarios which give the extremes in POCP values is to ensure that the selected scenarios will indicate the maximum and minimum POCP value that a certain species will ever have in any environment within Europe. The POCP values are thus represented by a span of values, referred to as POCP ranges, and not by site specific values. It makes it a bit more difficult to determine which is the most potent ozone producers between different VOC since the POCP ranges overlap for many species. There is however still a large difference in POCP ranges for the various VOC, which justifies the use of this ranking system instead of treating all VOC as a homogeneous group. The POCP ranges can thus be used to indicate the generally more potent ozone producers.

An alternative to the calculation of POCP ranges would be to calculate POCP values for a few typical scenarios, since it would not be practically possible to calculate POCP values for every possible chemical environment. In the case where typical scenarios are used, an actual environment of interest would always have to be compared to the best possible match among the available typical environments. However there would be differences between the actual environment and the chosen typical environment in almost all cases. This work has clearly shown that it is not possible to decide how much ozone a specific VOC will produce in a certain environment by comparing the amount of ozone the same VOC produces in another environment (Altenstedt and Pleijel, 1998). It is difficult to decide to what extent any differences between the actual chemical environment and the available typical environment will alter the representability of the POCP values. The use of POCP ranges, as suggested, is thus a much more robust and reliable tool which is more generally applicable for Europe than individual site specific POCP values.

In order to make a more detailed evaluation of the effects from an emission in a specific environment, site specific simulations are needed as a complement to the general methods. The use of POCP values and POCP ranges are not intended to quantify the absolute production of ozone, which to a large extent depends on the meteorological conditions.

6.3.2 Average and maximum changes in ozone production

The POCP ranges are presented both as average productions of ozone and as maximum changes in ozone concentration. The average production gives an indication of the total impact on the ozone concentration from a specific VOC and shows the impact on the background level of ozone. The maximum changes in concentration, on

the other hand, show the possible contribution from individual VOC on the peak ozone concentrations. Depending on whether the ozone peaks or the increased ozone background is of most interest, different sets of POCP ranges may be used. Some VOC react very fast in the troposphere and will give rise to a fast and high maximum change in ozone, while other more slowly reacting species will have a later and broader maximum change in ozone. In this case the average production of ozone may be fairly the same for the two types of VOC while the maximum changes in ozone concentration differ greatly. This was demonstrated previously in Figure 2.1, showing the change in ozone concentration from a point source of ethene, n-butane and o-xylene.

In Figure 6.5 the productions of ozone from a point source of ethene in different chemical environments are given both as average and maximum changes in ozone. The variations in ozone formation, from all other VOC tested in the study, are indicated as error bars. Figure 6.5 shows several important things. The absolute ozone formation varies depending on the chemical environment. The relation between the maximum and average ozone formation is not constant when the environment changes. The variation in ozone formed from other VOC than ethene varies, i.e. the POCP values vary, both if the environment changes and depending on whether average or maximum changes in ozone are studied.
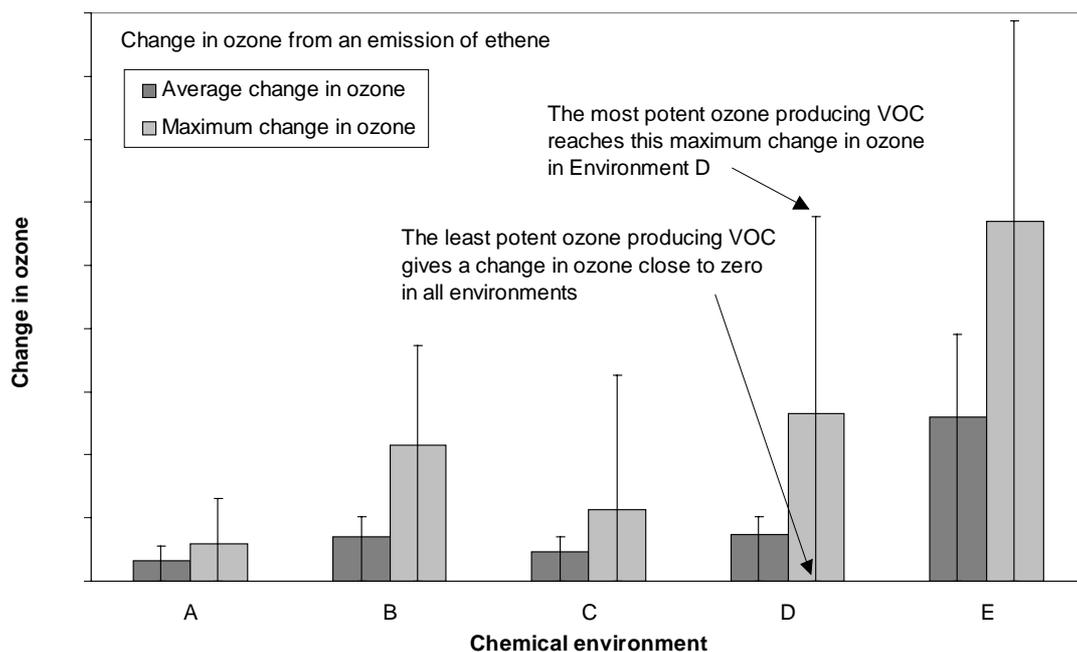
Figure 6.5   The production of ozone from ethene calculated as the average production of ozone* (darker bars) and as the maximum changes in ozone concentration (lighter bars) in five different chemical environments according to Table 5.1. The lines indicate the variation in ozone formation from all other VOC relative to the ozone formed from ethene. *Chapter 2.3.1 gives an explanation of how the average production of ozone is calculated.*

6.3.3 POCP ranges for use in Europe

Instead of showing site specific POCP values the results are presented as POCP ranges which are suggested to be applicable within Europe. Figure 6.6 explains how these ranges have been calculated and what they represent.
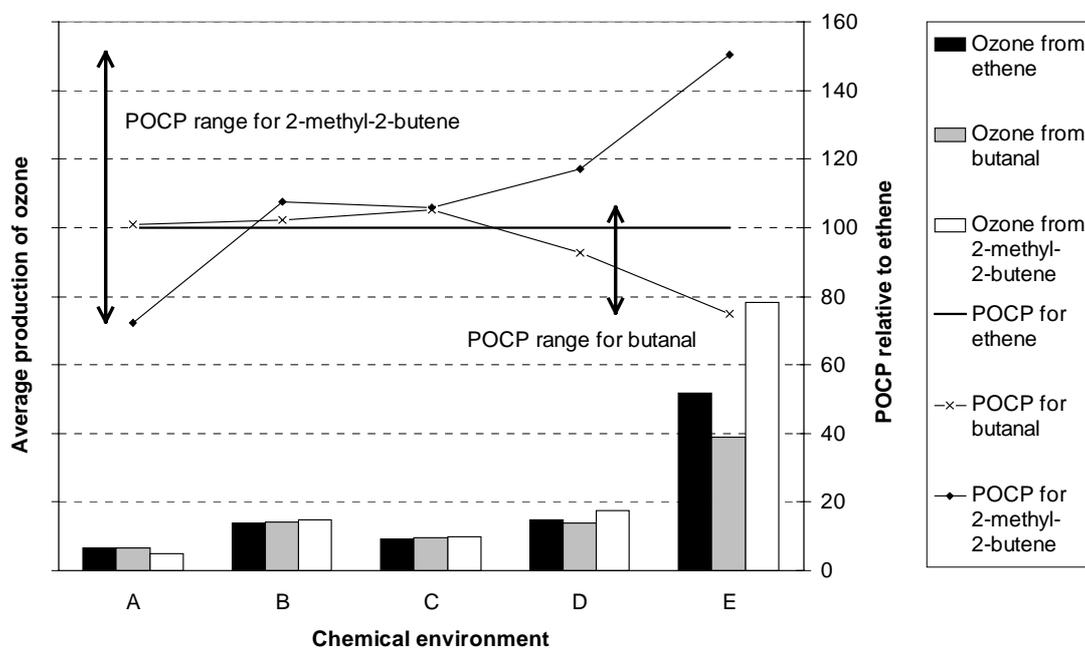
Figure 6.6   The relative and absolute average production of ozone* in five different chemical environments according to Table 5.1. The bars show the absolute production of ozone from ethene, butanal and 2-methyl-2-butene on the left y-axis. The relative POCP values are calculated relative to ethene (POCP = 100, straight line) and are given on the right y-axis as the connected points above the bars. The resulting POCP ranges which reaches from the minimum to the maximum POCP values are shown as vertical arrows for butanal and 2-methyl-2-butene. * *Chapter 2.3.1 gives an explanation of how the average production of ozone is calculated.*

For each VOC, the ozone production caused by a point source emission has been calculated both as the average production of ozone and as the maximum change in ozone concentration. These changes in ozone are the bars in Figure 6.6 When point sources for all 83 VOC have been tested, the individual changes in ozone from each VOC are compared to the ozone formed from a point source of ethene. Ethene is thus compared to itself and is given the relative POCP value 100. This normalisation versus ethene is performed for all environments so that ethene receives the POCP value 100 in all environments despite the fact that the absolute ozone formed from ethene varies from one environment to another. The relative POCP values are shown as the connected points above the bars in Figure 6.6. The POCP range of a VOC is defined as the values between the minimum and maximum POCP value in all environments. The ranges are indicated as vertical arrows in Figure 6.6 for butanal and 2-methyl-2-butene

In Figures 6.7 and 6.8, the POCP ranges are given for the 83 different VOC listed in Table 6.2. Figure 6.7 shows the POCP ranges based on the average ozone production

while Figure 6.8 shows the POCP ranges based on maximum changes in ozone. The ranges are indicated by the black bars.

The POCP ranges are given as numbers in Table A.1 in Appendix 1, which can be used if the numbers are difficult to determine correctly from the graphs.

In a choice between individual VOC, situations will certainly appear where the POCP ranges overlap for two different VOC. In such cases one can not be sure which one of the VOC that will produce more ozone in a real life situation. If the POCP ranges for two individual VOC are only shifted vertically relative to each other, as in the case of propane and butane in Figure 6.7, then there is a possibility that the VOC with the lower POCP range (propane) always has a lower POCP value than the VOC with the higher POCP range (butane). This can be checked through Tables A.2 - A.5 given in Appendix 1. An explanation of how this evaluation is done is given in Appendix 1.

The maximum changes in ozone concentration caused by an emission of a VOC will take place on different time scales depending on the reactivity of the VOC. For a highly reactive species, all of the VOC emitted in the point source will react fast and lead to a maximum during the same day as the emission occurs. For a slower reacting species the maximum may not come until several days after the emission. A plume of air from an emission source will be diluted as it moves further away from the emission source. A maximum which takes place close to the source of emission will thus be more concentrated than a maximum which does not happen until after a few days. In Figure 6.9 the maximum changes in ozone in the five chemical environments are given for all 83 VOC and the time of the maximum change in ozone is indicated through different symbols. Figures 6.8 and 6.9 are based on the same data set but the time of the maximum is only indicated in Figure 6.9.

Figure 6.7   POCP ranges shown as vertical bars for different VOC under European conditions. The values are based on the ***average ozone production**** and are calculated relative to ethene (POCP = 100). ** Chapter 2.3.1 gives an explanation of how the average production of ozone is calculated*

Figure 6.8   POCP ranges shown as vertical bars for different VOC under European conditions. The values are based on ***maximum changes in ozone concentration*** and are calculated relative to ethene (POCP = 100).

Figure 6.9   The relative maximum ozone formation for 83 different VOC compared to ethene. The time of the maximum change in ozone concentration is indicated through different symbols.

NOTE! 1,1-Dichloro-Ethene in **Figures 6.7-6.9** and in Tables in Appendix should be replaced by Dichloromethane.

POCP relative to ethene

Carbon Monoxide
Diethyl Disulfide
Diethyl Sulfide
Methyl Mercaptan
Tetrachloro-Ethene
Trichloro-Ethene
1,1,1-Trichloro-Ethane
1,2-Dichloro-Ethane
1,1-Dichloro-Ethane
1,1-Dichloro-Ethene
Acetic Acid
Methyl-t-Butyl-Ether
Diethyl-Ether
Dimethyl-Ether
s-Butyl-Acetate
n-Butyl-Acetate
Ethyl-Acetate
Methyl-Acetate
n-Butanol
i-Propanol
Ethanol
Methanol
Methyl-i-Butyl-Ketone
Ethyl-Methyl-Ketone
Acetone
Benzaldehyde
Methacrolein
Acrolein
Methyl-Glyoxal
Glyoxal
Valeraldehyde
i-Butyraldehyde
Butyraldehyde
Propionaldehyde
Acetaldehyde
Formaldehyde
i-Propyl-Benzene
n-Propyl-Benzene
o-Ethyl-Toluene
p-Ethyl-Toluene
m-Ethyl-Toluene
1,3,5-Trimethyl-Benzene
1,2,4-Trimethyl-Benzene
1,2,3-Trimethyl-Benzene
Ethyl-Benzene
p-Xylene
m-Xylene
o-Xylene
Toluene
Benzene
Acetylene (Ethyne)
Styrene
Isoprene
2-Methyl-2-Butene
2-Methyl-1-Butene
2-Pentene
1-Pentene
i-Butene
2-Butene
1-Butene
Propene
Ethene
Methyl-cyclo-Hexane
Dodecane
2-Methyl-Decane
Undecane
2-Methyl-Nonane
Decane
2-Methyl-Octane
Nonane
2-Methyl-Heptane
Octane
Heptane
3-Methyl-Pentane
2-Methyl-Pentane
Hexane
i-Pentane
Pentane
i-Butane
Butane
Propane
Ethane
Methane

POCP relative to ethene

Legend: ▲ Maximum day 1 ✕ Maximum day 2 ▪ Maximum day 3 or later

Species (left to right): Methane, Ethane, Propane, Butane, i-Butane, Pentane, i-Pentane, Hexane, 2-Methyl-Pentane, 3-Methyl-Pentane, Heptane, Octane, 2-Methyl-Heptane, Nonane, 2-Methyl-Octane, Decane, 2-Methyl-Nonane, Undecane, 2-Methyl-Decane, Dodecane, Methyl-cyclo-Hexane, Ethene, Propene, 1-Butene, 2-Butene, i-Butene, 1-Pentene, 2-Pentene, 2-Methyl-1-Butene, 2-Methyl-2-Butene, Isoprene, Styrene, Acetylene (Ethyne), Benzene, Toluene, o-Xylene, m-Xylene, p-Xylene, Ethyl-Benzene, 1,2,3-Trimethyl-Benzene, 1,2,4-Trimethyl-Benzene, 1,3,5-Trimethyl-Benzene, m-Ethyl-Toluene, p-Ethyl-Toluene, o-Ethyl-Toluene, n-Propyl-Benzene, i-Propyl-Benzene, Formaldehyde, Acetaldehyde, Propionaldehyde, Butyraldehyde, i-Butyraldehyde, Valeraldehyde, Glyoxal, Methyl-Glyoxal, Acrolein, Methacrolein, Benzaldehyde, Acetone, Ethyl-Methyl-Ketone, Methyl-i-Butyl-Ketone, Methanol, Ethanol, i-Propanol, n-Butanol, Methyl-Acetate, Ethyl-Acetate, n-Butyl-Acetate, s-Butyl-Acetate, Dimethyl-Ether, Diethyl-Ether, Methyl-t-Butyl-Ether, Acetic Acid, 1,1-Dichloro-Ethene, 1,1-Dichloro-Ethane, 1,2-Dichloro-Ethane, 1,1,1-Trichloro-Ethane, Trichloro-Ethene, Tetrachloro-Ethene, Methyl Mercaptan, Diethyl Sulfide, Diethyl Disulfide, Carbon Monoxide

7 Discussion and conclusions

The POCP values for 83 different VOC are presented in the form of ranges and not as site specific values. The POCP ranges can be considered as POCP values including error estimates and are therefore more generally applicable than site specific POCP values. The POCP ranges should however not be expressed as the mean value of the range plus or minus a certain interval. It is clear from Figure 6.9 that the mean values of the ranges are not equal to the mean values calculated from individual data points, since the individual data points are not evenly distributed over the ranges.

The use of POCP ranges, as suggested, is a much more robust and reliable tool than individual site specific POCP values. The ranges are based on the extremes of the POCP values and are constructed with the intention to include all POCP values an individual VOC will have in any European environment where ozone formation is of environmental concern. The five chemical environments should not be considered as individual typical scenarios with their own individual set of POCP values and they should not be applied separately in real life situations which seem similar to the typical ones. Different local conditions may have such an impact that the POCP values of the selected environment do not reflect the actual situation. The use of POCP ranges avoids these type of errors.

The calculated POCP ranges show that the most efficient ozone producers, based on the average ozone production, are isoprene and 2-methyl-2-butene. The largest maximum changes in ozone concentration are caused by 2-methyl-2-butene and acrolein. As a group, the alkenes are the most potent ozone producers followed by alkanes and then the aromatics in all environments except in a highly polluted environment (environment E). Here, many aromatics produce more ozone than the alkanes but the alkenes are still the most efficient ozone producers. A previous study of POCP values using the IVL model has shown results similar to these but the most ozone producing species were then found to be ethene and acrolein followed by other higher alkenes, aromatics and alkanes (Andersson-Sköld et al. 1992). A recent study of POCP values, performed for the conditions in north west Europe, points out the aromatics as the most potent ozone producers (Derwent et al. 1998). The chemical environment in that study is highly polluted and describes a high NO_x scenario. The highly polluted environment in this study (environment E), which produces higher POCP values for aromatics than for alkanes, also describes high NO_x conditions which thus agree with the results from Derwent et al. (1998). Other explanations to the observed differences in POCP ranking is, apart from the impact of different chemical environments, the use of a different chemical scheme. The chemical scheme used by Derwent et al. (1998) includes around 120 VOC and thus contains more chemical reactions than the IVL chemical scheme, used in this study.

Even though the POCP ranges overlap for many species there are still large differences in the ozone production from different VOC, which justifies the use of a ranking scale instead of treating all VOC as a homogeneous group of species in abatement strategies. The use of POCP ranges is considered to be a robust and reliable tool by which decisions on VOC emission reductions can be based in order to minimise ground level ozone production.

8   Acknowledgements

9   References

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Appendix

The POCP ranges for 83 different VOC are given in Figures 6.7 (average production of ozone) and 6.8 (maximum changes in ozone concentration). The POCP ranges presented in the figures are also given as numbers in Table A.1.

In a situation where the POCP ranges for two different VOC overlap it is not possible to determine directly from the POCP ranges which of the VOC is the most potent ozone producer. If the POCP ranges for two individual VOC are only shifted vertically relative to each other, as in the case of propane and butane in Figure 6.7, there is a probability that the VOC with the lower POCP range (propane) always has a lower POCP value than the VOC with the higher POCP range (butane). This can be checked through Tables A.2 - A.5.

In Tables A.2 - A.5 the ordering of the 83 different VOC are given for all five chemical environments. Tables A.2 and A.3 give the ranking based on average ozone productions while Tables A.4 and A.5 give the ranking based on maximum changes in ozone concentration. In Table A.2 and A.4 the different VOC are listed in the same order as in Table 4.2 in the report together with their relative ranking as ozone producers compared to the other 82 VOC. In Table A.3 and A.5 the different VOC are listed according to their ozone formation so that the most potent ozone producers are given at the top of the table while the VOC which produce very little ozone are at the bottom of the table.

In the example with propane and butane, if their average productions of ozone are compared, their relative ranking versus each other can be checked through Tables A.2 or A.3. In Table A.2 we check the ranking of propane which is number 59, 44, 57, 47 and 59 respectively in the five chemical environments. This means that propane is the 59th most ozone producing VOC out of the 83 tested VOC in environment A and the 44th most ozone producing VOC in environment B and so on. The ranking for butane is 42, 33, 38, 34 and 53 which means that butane will always form more ozone than propane since it is ranked higher in all environments (42<59, 33<44, 38<58, 38<47 and 53<59). The same information can be extracted from Table A.3 through finding propane in each column and then checking whether butane lies above or below for each individual column.

The ranking between two species may not stay constant when checked through the Tables. If i-pentane is compared with butane in Figure 6.7 the situation is similar to the case when butane was compared to propane. Checking the ranking for i-pentane in Table A.2 one finds 68, 52, 61, 46 and 49. Thus butane produces more ozone than i-pentane in all environments except E. It is therefore not possible to decide which one is the most potent ozone producer without a further site specific evaluation. Table A.3 and A.5 can also be used to easily find the VOC which gives the largest and the least ozone production in the different chemical environments.

Table A.1 The POCP ranges for VOC based on average and maximum changes in ozone.		POCP ranges relative to ethene			
		Average ozone production		Maximum change in ozone concentration	
Group	VOC	From	To	From	To
Alkanes	Methane	0.5	1.2	0.5	1.3
	Ethane	14	36	13	23
	Propane	39	71	29	49
	Butane	53	92	43	71
	i-Butane	47	69	32	57
	Pentane	73	116	63	106
	i-Pentane	25	65	30	58
	Hexane	81	128	72	119
	2-Methyl-Pentane	69	96	55	87
	3-Methyl-Pentane	73	108	61	98
	Heptane	76	123	68	124
	Octane	74	122	67	140
	2-Methyl-Heptane	71	103	57	90
	Nonane	73	121	65	125
	2-Methyl-Octane	71	104	56	96
	Decane	72	118	62	117
	2-Methyl-Nonane	71	105	55	93
	Undecane	69	115	57	113
	2-Methyl-Decane	70	106	53	94
	Dodecane	70	114	53	89
	Methyl-cyclo-Hexane	38	112	36	125
Alkenes	Ethene	100	100	100	100
	Propene	117	133	114	142
	1-Butene	115	137	113	134
	2-Butene	100	127	110	158
	i-Butene	86	104	79	128
	1-Pentene	107	135	95	123
	2-Pentene	116	141	122	182
	2-Methyl-1-Butene	94	101	78	106
	2-Methyl-2-Butene	72	151	71	290
	Isoprene	134	169	133	190
	Styrene	76	100	73	108
Alkynes	Acetylene (Ethyne)	26	59	22	45
Aromatics	Benzene	23	47	18	37
	Toluene	30	67	25	65
	o-Xylene	61	89	61	92
	m-Xylene	102	114	89	118
	p-Xylene	96	110	76	115
	Ethyl-Benzene	74	90	53	85
	1,2,3-Trimethyl-Benzene	58	66	59	68
	1,2,4-Trimethyl-Benzene	75	87	78	97
	1,3,5-Trimethyl-Benzene	59	68	63	85
	m-Ethyl-Toluene	94	108	72	110
	p-Ethyl-Toluene	94	97	67	98
	o-Ethyl-Toluene	61	64	45	64
	n-Propyl-Benzene	70	89	52	76
	i-Propyl-Benzene	59	67	37	61
Aldehydes	Formaldehyde	18	55	25	83
	Acetaldehyde	68	80	67	92
	Propionaldehyde	74	99	70	107
	Butyraldehyde	75	105	70	106
	i-Butyraldehyde	53	65	35	65
	Valeraldehyde	74	106	67	98
	Glyoxal	17	22	18	22
	Methyl-Glyoxal	52	91	66	130
	Acrolein	73	126	73	219
	Methacrolein	94	110	109	134
	Benzaldehyde	0.0	0.0	0.0	2.1
Ketones	Acetone	35	53	21	53
	Ethyl-Methyl-Ketone	57	61	33	58
	Methyl-i-Butyl-Ketone	65	89	49	96
Alcohols	Methanol	13	21	10	16
	Ethanol	44	63	36	57
	i-Propanol	37	43	23	38
	n-Butanol	63	95	57	91
Esters	Methyl-Acetate	4.1	9.6	3.2	5.9
	Ethyl-Acetate	7.4	40	7.8	34
	n-Butyl-Acetate	22	66	23	60
	s-Butyl-Acetate	12	49	15	40
Ethers and organic acids	Dimethyl-Ether	18	48	17	43
	Diethyl-Ether	25	80	21	66
	Methyl-t-Butyl-Ether	42	56	29	46
	Acetic Acid	11	20	8.0	13
Chlorocarbons	1,1-Dichloro-Ethene	1.1	3.5	1.0	2.5
	1,1-Dichloro-Ethane	3.8	12	3.3	9.5
	1,2-Dichloro-Ethane	0.0	0.0	0.0	2.8
	1,1,1-Trichloro-Ethane	0.1	0.3	0.1	1.3
	Trichloro-Ethene	5.6	15	5.5	13
	Tetrachloro-Ethene	0.7	2.0	0.5	1.4
Others	Methyl Mercaptan	60	64	63	122
	Diethyl Sulfide	50	74	41	71
	Diethyl Disulfide	34	38	38	110
	Carbon Monoxide	2.3	5.3	1.9	3.3

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Table A.2 The ranking of VOC according to ozone formation ability based on the *average ozone production* in the five chemical environments.

Group	VOC	Ranking in environment				
		A	B	C	D	E
Alkanes	Methane	80	80	80	80	80
	Ethane	69	66	70	68	70
	Propane	59	44	57	47	59
	Butane	42	33	38	34	53
	i-Butane	54	45	48	45	56
	Pentane	15	13	12	12	28
	i-Pentane	68	52	61	46	49
	Hexane	5	7	6	7	19
	2-Methyl-Pentane	28	30	31	30	38
	3-Methyl-Pentane	17	17	14	18	30
	Heptane	11	8	8	8	21
	Octane	6	10	9	10	25
	2-Methyl-Heptane	36	22	23	23	32
	Nonane	14	9	10	11	27
	2-Methyl-Octane	27	20	21	25	33
	Decane	18	11	11	13	31
	2-Methyl-Nonane	31	18	22	22	34
	Undecane	24	12	13	14	39
	2-Methyl-Decane	32	16	24	21	35
	Dodecane	30	14	15	16	37
	Methyl-cyclo-Hexane	10	43	41	50	60
Alkenes	Ethene	21	26	25	17	11
	Propene	7	5	5	4	4
	1-Butene	4	3	3	3	5
	2-Butene	20	6	7	9	6
	i-Butene	37	37	37	31	10
	1-Pentene	2	4	4	5	8
	2-Pentene	8	2	2	2	3
	2-Methyl-1-Butene	29	25	29	19	13
	2-Methyl-2-Butene	44	15	17	6	1
	Isoprene	1	1	1	1	2
	Styrene	22	32	34	36	20
Alkynes	Acetylene (Ethyne)	56	59	60	60	63
Aromatics	Benzene	65	62	64	63	65
	Toluene	67	47	51	43	44
	o-Xylene	51	38	40	35	17
	m-Xylene	9	19	19	15	7
	p-Xylene	12	27	26	24	12
	Ethyl-Benzene	34	36	35	37	23
	1,2,3-Trimethyl-Benzene	46	58	56	56	46
	1,2,4-Trimethyl-Benzene	41	42	43	40	18
	1,3,5-Trimethyl-Benzene	48	55	55	54	40
	m-Ethyl-Toluene	16	23	20	20	14
	p-Ethyl-Toluene	25	28	30	28	15
	o-Ethyl-Toluene	47	49	49	49	47
	n-Propyl-Benzene	38	35	36	38	36
	i-Propyl-Benzene	50	46	46	48	48
Aldehydes	Formaldehyde	70	70	69	65	52
	Acetaldehyde	40	41	42	42	41
	Propionaldehyde	23	29	27	32	24
	Butyraldehyde	19	24	18	29	22
	i-Butyraldehyde	57	48	54	57	51
	Valeraldehyde	26	21	16	26	26
	Glyoxal	71	71	71	72	67
	Methyl-Glyoxal	58	57	52	44	16
	Acrolein	3	40	33	39	29
	Methacrolein	13	31	28	27	9
	Benzaldehyde	83	83	83	83	82
Ketones	Acetone	66	65	67	64	54
	Ethyl-Methyl-Ketone	53	54	58	52	50
	Methyl-i-Butyl-Ketone	35	39	39	41	42
Alcohols	Methanol	74	72	73	71	69
	Ethanol	52	50	50	53	57
	i-Propanol	63	63	63	62	62
	n-Butanol	33	34	32	33	43
Esters	Methyl-Acetate	76	76	76	76	75
	Ethyl-Acetate	62	68	68	70	73
	n-Butyl-Acetate	45	61	53	61	66
	s-Butyl-Acetate	60	64	62	67	71
Ethers and organic acids	Dimethyl-Ether	61	69	65	69	68
	Diethyl-Ether	39	51	44	58	64
	Methyl-t-Butyl-Ether	55	60	59	59	58
	Acetic Acid	73	73	72	73	72
Chlorocarbons	1,1-Dichloro-Ethene	78	78	78	78	78
	1,1-Dichloro-Ethane	75	74	75	75	76
	1,2-Dichloro-Ethane	82	82	82	82	83
	1,1,1-Trichloro-Ethane	81	81	81	81	81
	Trichloro-Ethene	72	75	74	74	74
	Tetrachloro-Ethene	79	79	79	79	79
Others	Methyl Mercaptan	49	53	47	51	45
	Diethyl Sulfide	43	56	45	55	55
	Diethyl Disulfide	64	67	66	66	61
	Carbon Monoxide	77	77	77	77	77

Table A.3   The ranking of VOC according to ozone formation ability based on the *average ozone production* in the five chemical environments.

	Ranking of VOC in environment				
Ranking	A	B	C	D	E
1	Isoprene	Isoprene	Isoprene	Isoprene	2-Methyl-2-Butene
2	1-Pentene	2-Pentene	2-Pentene	2-Pentene	Isoprene
3	Acrolein	1-Butene	1-Butene	1-Butene	2-Pentene
4	1-Butene	1-Pentene	1-Pentene	Propene	Propene
5	Hexane	Propene	Propene	1-Pentene	1-Butene
6	Octane	2-Butene	Hexane	2-Methyl-2-Butene	2-Butene
7	Propene	Hexane	2-Butene	Hexane	m-Xylene
8	2-Pentene	Heptane	Heptane	Heptane	1-Pentene
9	m-Xylene	Nonane	Octane	2-Butene	Methacrolein
10	Methyl-cyclo-Hexane	Octane	Nonane	Octane	i-Butene
11	Heptane	Decane	Decane	Nonane	Ethene
12	p-Xylene	Undecane	Pentane	Pentane	p-Xylene
13	Methacrolein	Pentane	Undecane	Decane	2-Methyl-1-Butene
14	Nonane	Dodecane	3-Methyl-Pentane	Undecane	m-Ethyl-Toluene
15	Pentane	2-Methyl-2-Butene	Dodecane	m-Xylene	p-Ethyl-Toluene
16	m-Ethyl-Toluene	2-Methyl-Decane	Valeraldehyde	Dodecane	Methyl-Glyoxal
17	3-Methyl-Pentane	3-Methyl-Pentane	2-Methyl-2-Butene	Ethene	o-Xylene
18	Decane	2-Methyl-Nonane	Butyraldehyde	3-Methyl-Pentane	1,2,4-Trimethyl-Benzene
19	Butyraldehyde	m-Xylene	m-Xylene	2-Methyl-1-Butene	Hexane
20	2-Butene	2-Methyl-Octane	m-Ethyl-Toluene	m-Ethyl-Toluene	Styrene
21	Ethene	Valeraldehyde	2-Methyl-Octane	2-Methyl-Decane	Heptane
22	Styrene	2-Methyl-Heptane	2-Methyl-Nonane	2-Methyl-Nonane	Butyraldehyde
23	Propionaldehyde	m-Ethyl-Toluene	2-Methyl-Heptane	2-Methyl-Heptane	Ethyl-Benzene
24	Undecane	Butyraldehyde	2-Methyl-Decane	p-Xylene	Propionaldehyde
25	p-Ethyl-Toluene	2-Methyl-1-Butene	Ethene	2-Methyl-Octane	Octane
26	Valeraldehyde	Ethene	p-Xylene	Valeraldehyde	Valeraldehyde
27	2-Methyl-Octane	p-Xylene	Propionaldehyde	Methacrolein	Nonane
28	2-Methyl-Pentane	p-Ethyl-Toluene	Methacrolein	p-Ethyl-Toluene	Pentane
29	2-Methyl-1-Butene	Propionaldehyde	2-Methyl-1-Butene	Butyraldehyde	Acrolein
30	Dodecane	2-Methyl-Pentane	p-Ethyl-Toluene	2-Methyl-Pentane	3-Methyl-Pentane
31	2-Methyl-Nonane	Methacrolein	2-Methyl-Pentane	i-Butene	Decane
32	2-Methyl-Decane	Styrene	n-Butanol	Propionaldehyde	2-Methyl-Heptane
33	n-Butanol	Butane	Acrolein	n-Butanol	2-Methyl-Octane
34	Ethyl-Benzene	n-Butanol	Styrene	Butane	2-Methyl-Nonane
35	Methyl-i-Butyl-Ketone	n-Propyl-Benzene	Ethyl-Benzene	o-Xylene	2-Methyl-Decane
36	2-Methyl-Heptane	Ethyl-Benzene	n-Propyl-Benzene	Styrene	n-Propyl-Benzene
37	i-Butene	i-Butene	i-Butene	Ethyl-Benzene	Dodecane
38	n-Propyl-Benzene	o-Xylene	Butane	n-Propyl-Benzene	2-Methyl-Pentane
39	Diethyl-Ether	Methyl-i-Butyl-Ketone	Methyl-i-Butyl-Ketone	Acrolein	Undecane
40	Acetaldehyde	Acrolein	o-Xylene	1,2,4-Trimethyl-Benzene	1,3,5-Trimethyl-Benzene
41	1,2,4-Trimethyl-Benzene	Acetaldehyde	Methyl-cyclo-Hexane	Methyl-i-Butyl-Ketone	Acetaldehyde
42	Butane	1,2,4-Trimethyl-Benzene	Acetaldehyde	Acetaldehyde	Methyl-i-Butyl-Ketone
43	Diethyl Sulfide	Methyl-cyclo-Hexane	1,2,4-Trimethyl-Benzene	Toluene	n-Butanol
44	2-Methyl-2-Butene	Propane	Diethyl-Ether	Methyl-Glyoxal	Toluene
45	n-Butyl-Acetate	i-Butane	Diethyl Sulfide	i-Butane	Methyl Mercaptan
46	1,2,3-Trimethyl-Benzene	i-Propyl-Benzene	i-Propyl-Benzene	i-Pentane	1,2,3-Trimethyl-Benzene
47	o-Ethyl-Toluene	Toluene	Methyl Mercaptan	Propane	o-Ethyl-Toluene
48	1,3,5-Trimethyl-Benzene	i-Butyraldehyde	i-Butane	i-Propyl-Benzene	i-Propyl-Benzene
49	Methyl Mercaptan	o-Ethyl-Toluene	o-Ethyl-Toluene	o-Ethyl-Toluene	i-Pentane
50	i-Propyl-Benzene	Ethanol	Ethanol	Methyl-cyclo-Hexane	Ethyl-Methyl-Ketone
51	o-Xylene	Diethyl-Ether	Toluene	Methyl Mercaptan	i-Butyraldehyde
52	Ethanol	i-Pentane	Methyl-Glyoxal	Ethyl-Methyl-Ketone	Formaldehyde
53	Ethyl-Methyl-Ketone	Methyl Mercaptan	n-Butyl-Acetate	Ethanol	Butane
54	i-Butane	Ethyl-Methyl-Ketone	i-Butyraldehyde	1,3,5-Trimethyl-Benzene	Acetone
55	Methyl-t-Butyl-Ether	1,3,5-Trimethyl-Benzene	1,3,5-Trimethyl-Benzene	Diethyl Sulfide	Diethyl Sulfide
56	Acetylene (Ethyne)	Diethyl Sulfide	1,2,3-Trimethyl-Benzene	1,2,3-Trimethyl-Benzene	i-Butane
57	i-Butyraldehyde	Methyl-Glyoxal	Propane	i-Butyraldehyde	Ethanol
58	Methyl-Glyoxal	1,2,3-Trimethyl-Benzene	Ethyl-Methyl-Ketone	Methyl-t-Butyl-Ether	Methyl-t-Butyl-Ether
59	Propane	Acetylene (Ethyne)	Methyl-t-Butyl-Ether	Methyl-t-Butyl-Ether	Propane
60	s-Butyl-Acetate	Methyl-t-Butyl-Ether	Acetylene (Ethyne)	Acetylene (Ethyne)	Methyl-cyclo-Hexane
61	Dimethyl-Ether	n-Butyl-Acetate	i-Pentane	n-Butyl-Acetate	Diethyl Disulfide
62	Ethyl-Acetate	Benzene	s-Butyl-Acetate	i-Propanol	i-Propanol
63	i-Propanol	i-Propanol	i-Propanol	Benzene	Acetylene (Ethyne)
64	Diethyl Disulfide	s-Butyl-Acetate	Benzene	Acetone	Diethyl-Ether
65	Benzene	Acetone	Dimethyl-Ether	Formaldehyde	Benzene
66	Acetone	Ethane	Diethyl Disulfide	Diethyl Disulfide	n-Butyl-Acetate
67	Toluene	Diethyl Disulfide	Acetone	s-Butyl-Acetate	Glyoxal
68	i-Pentane	Ethyl-Acetate	Ethyl-Acetate	Ethane	Dimethyl-Ether
69	Ethane	Dimethyl-Ether	Formaldehyde	Dimethyl-Ether	Methanol
70	Formaldehyde	Formaldehyde	Ethane	Ethyl-Acetate	Ethane
71	Glyoxal	Glyoxal	Glyoxal	Methanol	s-Butyl-Acetate
72	Trichloro-Ethene	Methanol	Acetic Acid	Glyoxal	Acetic Acid
73	Acetic Acid	Acetic Acid	Methanol	Acetic Acid	Ethyl-Acetate
74	Methanol	1,1-Dichloro-Ethane	Trichloro-Ethene	Trichloro-Ethene	Trichloro-Ethene
75	1,1-Dichloro-Ethane	Trichloro-Ethene	1,1-Dichloro-Ethane	1,1-Dichloro-Ethane	Methyl-Acetate
76	Methyl-Acetate	Methyl-Acetate	Methyl-Acetate	Methyl-Acetate	1,1-Dichloro-Ethane
77	Carbon Monoxide	Carbon Monoxide	Carbon Monoxide	Carbon Monoxide	Carbon Monoxide
78	1,1-Dichloro-Ethene	1,1-Dichloro-Ethene	1,1-Dichloro-Ethene	1,1-Dichloro-Ethene	1,1-Dichloro-Ethene
79	Tetrachloro-Ethene	Tetrachloro-Ethene	Tetrachloro-Ethene	Tetrachloro-Ethene	Tetrachloro-Ethene
80	Methane	Methane	Methane	Methane	Methane
81	1,1,1-Trichloro-Ethane	1,1,1-Trichloro-Ethane	1,1,1-Trichloro-Ethane	1,1,1-Trichloro-Ethane	1,1,1-Trichloro-Ethane
82	1,2-Dichloro-Ethane	1,2-Dichloro-Ethane	1,2-Dichloro-Ethane	1,2-Dichloro-Ethane	Benzaldehyde
83	Benzaldehyde	Benzaldehyde	Benzaldehyde	Benzaldehyde	1,2-Dichloro-Ethane

Table A.4 The ranking of VOC according to ozone formation ability based on *maximum changes in ozone concentration* in the five chemical environments.

Group	VOC	A	B	C	D	E
Alkanes	Methane	80	80	82	80	79
	Ethane	70	71	71	71	71
	Propane	58	58	60	61	62
	Butane	43	50	51	49	55
	i-Butane	56	59	58	58	57
	Pentane	20	35	29	33	27
	i-Pentane	67	61	61	55	49
	Hexane	11	22	19	21	19
	2-Methyl-Pentane	36	47	42	41	38
	3-Methyl-Pentane	25	34	32	36	25
	Heptane	7	28	22	27	20
	Octane	3	27	17	28	21
	2-Methyl-Heptane	34	44	40	39	30
	Nonane	5	25	20	32	22
	2-Methyl-Octane	27	41	33	40	29
	Decane	13	29	23	34	26
	2-Methyl-Nonane	31	42	35	42	31
	Undecane	16	31	28	38	35
	2-Methyl-Decane	29	43	38	45	36
	Dodecane	35	38	36	44	39
	Methyl-cyclo-Hexane	6	48	46	52	61
Alkenes	Ethene	22	12	21	11	11
	Propene	15	5	6	5	4
	1-Butene	9	8	7	8	6
	2-Butene	17	4	5	4	5
	i-Butene	39	10	8	10	12
	1-Pentene	8	9	10	14	8
	2-Pentene	10	3	2	2	2
	2-Methyl-1-Butene	40	14	15	16	16
	2-Methyl-2-Butene	45	1	1	1	1
	Isoprene	2	2	4	3	3
	Styrene	26	13	13	17	37
Alkynes	Acetylene (Ethyne)	60	63	64	65	64
Aromatics	Benzene	63	66	67	68	65
	Toluene	69	53	56	51	43
	o-Xylene	52	32	43	26	17
	m-Xylene	12	16	18	12	9
	p-Xylene	14	21	26	20	10
	Ethyl-Benzene	37	40	44	43	23
	1,2,3-Trimethyl-Benzene	46	45	48	31	48
	1,2,4-Trimethyl-Benzene	38	23	34	13	18
	1,3,5-Trimethyl-Benzene	42	33	47	18	40
	m-Ethyl-Toluene	18	19	25	22	15
	p-Ethyl-Toluene	24	24	30	29	14
	o-Ethyl-Toluene	51	49	52	48	46
	n-Propyl-Benzene	41	46	45	46	32
	i-Propyl-Benzene	54	54	53	53	47
Aldehydes	Formaldehyde	68	36	31	19	50
	Acetaldehyde	32	30	27	23	42
	Propionaldehyde	19	18	14	25	33
	Butyraldehyde	21	17	16	24	28
	i-Butyraldehyde	50	51	49	56	52
	Valeraldehyde	23	20	24	30	24
	Glyoxal	71	70	70	69	67
	Methyl-Glyoxal	48	15	37	7	13
	Acrolein	1	6	3	9	34
	Methacrolein	4	7	9	6	7
	Benzaldehyde	83	83	79	81	81
Ketones	Acetone	66	68	69	59	53
	Ethyl-Methyl-Ketone	57	60	59	57	51
	Methyl-i-Butyl-Ketone	28	39	41	47	44
Alcohols	Methanol	74	72	72	72	69
	Ethanol	55	55	55	54	56
	i-Propanol	65	64	66	64	59
	n-Butanol	33	37	39	37	41
Esters	Methyl-Acetate	76	76	76	76	75
	Ethyl-Acetate	64	69	68	70	73
	n-Butyl-Acetate	53	56	54	60	63
	s-Butyl-Acetate	62	67	65	67	70
Ethers and organic acids	Dimethyl-Ether	61	65	63	66	68
	Diethyl-Ether	49	57	57	63	66
	Methyl-t-Butyl-Ether	59	62	62	62	58
	Acetic Acid	73	73	73	73	72
Chlorocarbons	1,1-Dichloro-Ethene	78	78	80	78	78
	1,1-Dichloro-Ethane	75	75	75	75	76
	1,2-Dichloro-Ethane	81	81	77	82	83
	1,1,1-Trichloro-Ethane	82	82	83	83	82
	Trichloro-Ethene	72	74	74	74	74
	Tetrachloro-Ethene	79	79	81	79	80
Others	Methyl Mercaptan	30	11	11	15	45
	Diethyl Sulfide	44	52	50	50	54
	Diethyl Disulfide	47	26	12	35	60
	Carbon Monoxide	77	77	78	77	77

Table A.5 The ranking of VOC according to ozone formation ability based on *maximum changes in ozone concentration* in the five chemical environments.

	Ranking of VOC in environment				
Ranking	A	B	C	D	E
1	Acrolein	2-Methyl-2-Butene	2-Methyl-2-Butene	2-Methyl-2-Butene	2-Methyl-2-Butene
2	Isoprene	Isoprene	2-Pentene	2-Pentene	2-Pentene
3	Octane	2-Pentene	Acrolein	Isoprene	Isoprene
4	Methacrolein	2-Butene	Isoprene	2-Butene	Propene
5	Nonane	Propene	2-Butene	Propene	2-Butene
6	Methyl-cyclo-Hexane	Acrolein	Propene	Methacrolein	1-Butene
7	Heptane	Methacrolein	1-Butene	Methyl-Glyoxal	Methacrolein
8	1-Pentene	1-Butene	i-Butene	1-Butene	1-Pentene
9	1-Butene	1-Pentene	Methacrolein	Acrolein	m-Xylene
10	2-Pentene	i-Butene	1-Pentene	i-Butene	p-Xylene
11	Hexane	Methyl Mercaptan	Methyl Mercaptan	Ethene	Ethene
12	m-Xylene	Ethene	Diethyl Disulfide	m-Xylene	i-Butene
13	Decane	Styrene	Styrene	1,2,4-Trimethyl-Benzene	Methyl-Glyoxal
14	p-Xylene	2-Methyl-1-Butene	Propionaldehyde	1-Pentene	p-Ethyl-Toluene
15	Propene	Methyl-Glyoxal	2-Methyl-1-Butene	Methyl Mercaptan	m-Ethyl-Toluene
16	Undecane	m-Xylene	Butyraldehyde	2-Methyl-1-Butene	2-Methyl-1-Butene
17	2-Butene	Butyraldehyde	Octane	Styrene	o-Xylene
18	m-Ethyl-Toluene	Propionaldehyde	m-Xylene	1,3,5-Trimethyl-Benzene	1,2,4-Trimethyl-Benzene
19	Propionaldehyde	m-Ethyl-Toluene	Hexane	Formaldehyde	Hexane
20	Pentane	Valeraldehyde	Nonane	p-Xylene	Heptane
21	Butyraldehyde	p-Xylene	Ethene	Hexane	Octane
22	Ethene	Hexane	Heptane	m-Ethyl-Toluene	Nonane
23	Valeraldehyde	1,2,4-Trimethyl-Benzene	Decane	Acetaldehyde	Ethyl-Benzene
24	p-Ethyl-Toluene	p-Ethyl-Toluene	Valeraldehyde	Butyraldehyde	Valeraldehyde
25	3-Methyl-Pentane	Nonane	m-Ethyl-Toluene	Propionaldehyde	3-Methyl-Pentane
26	Styrene	Diethyl Disulfide	p-Xylene	o-Xylene	Decane
27	2-Methyl-Octane	Octane	Acetaldehyde	Heptane	Pentane
28	Methyl-i-Butyl-Ketone	Heptane	Undecane	Octane	Butyraldehyde
29	2-Methyl-Decane	Decane	Pentane	p-Ethyl-Toluene	2-Methyl-Octane
30	Methyl Mercaptan	Acetaldehyde	p-Ethyl-Toluene	Valeraldehyde	2-Methyl-Heptane
31	2-Methyl-Nonane	Undecane	Formaldehyde	1,2,3-Trimethyl-Benzene	2-Methyl-Nonane
32	Acetaldehyde	o-Xylene	3-Methyl-Pentane	Nonane	n-Propyl-Benzene
33	n-Butanol	1,3,5-Trimethyl-Benzene	2-Methyl-Octane	Pentane	Propionaldehyde
34	2-Methyl-Heptane	3-Methyl-Pentane	1,2,4-Trimethyl-Benzene	Decane	Acrolein
35	Dodecane	Pentane	2-Methyl-Nonane	Diethyl Disulfide	Undecane
36	2-Methyl-Pentane	Formaldehyde	Dodecane	3-Methyl-Pentane	2-Methyl-Decane
37	Ethyl-Benzene	n-Butanol	Methyl-Glyoxal	n-Butanol	Styrene
38	1,2,4-Trimethyl-Benzene	Dodecane	2-Methyl-Decane	Undecane	2-Methyl-Pentane
39	i-Butene	Methyl-i-Butyl-Ketone	n-Butanol	2-Methyl-Heptane	Dodecane
40	2-Methyl-1-Butene	Ethyl-Benzene	2-Methyl-Heptane	2-Methyl-Octane	1,3,5-Trimethyl-Benzene
41	n-Propyl-Benzene	2-Methyl-Octane	Methyl-i-Butyl-Ketone	2-Methyl-Pentane	n-Butanol
42	1,3,5-Trimethyl-Benzene	2-Methyl-Nonane	2-Methyl-Nonane	2-Methyl-Nonane	Acetaldehyde
43	Butane	2-Methyl-Decane	o-Xylene	Ethyl-Benzene	Toluene
44	Diethyl Sulfide	2-Methyl-Heptane	Ethyl-Benzene	Dodecane	Methyl-i-Butyl-Ketone
45	2-Methyl-2-Butene	1,2,3-Trimethyl-Benzene	n-Propyl-Benzene	2-Methyl-Decane	Methyl Mercaptan
46	1,2,3-Trimethyl-Benzene	n-Propyl-Benzene	Methyl-cyclo-Hexane	n-Propyl-Benzene	o-Ethyl-Toluene
47	Diethyl Disulfide	2-Methyl-Pentane	1,3,5-Trimethyl-Benzene	Methyl-i-Butyl-Ketone	i-Propyl-Benzene
48	Methyl-Glyoxal	Methyl-cyclo-Hexane	1,2,3-Trimethyl-Benzene	o-Ethyl-Toluene	1,2,3-Trimethyl-Benzene
49	Diethyl-Ether	o-Ethyl-Toluene	i-Butyraldehyde	Butane	i-Pentane
50	i-Butyraldehyde	Butane	Diethyl Sulfide	Diethyl Sulfide	Formaldehyde
51	o-Ethyl-Toluene	i-Butyraldehyde	Butane	Toluene	Ethyl-Methyl-Ketone
52	o-Xylene	Diethyl Sulfide	o-Ethyl-Toluene	Methyl-cyclo-Hexane	i-Butyraldehyde
53	n-Butyl-Acetate	Toluene	i-Propyl-Benzene	i-Propyl-Benzene	Acetone
54	i-Propyl-Benzene	i-Propyl-Benzene	n-Butyl-Acetate	Ethanol	Diethyl Sulfide
55	Ethanol	Ethanol	Ethanol	i-Pentane	Butane
56	i-Butane	n-Butyl-Acetate	Toluene	i-Butyraldehyde	Ethanol
57	Ethyl-Methyl-Ketone	Diethyl-Ether	Diethyl-Ether	Ethyl-Methyl-Ketone	i-Butane
58	Propane	Propane	i-Butane	i-Butane	Methyl-t-Butyl-Ether
59	Methyl-t-Butyl-Ether	i-Butane	Ethyl-Methyl-Ketone	Acetone	i-Propanol
60	Acetylene (Ethyne)	Ethyl-Methyl-Ketone	Propane	n-Butyl-Acetate	Diethyl Disulfide
61	Dimethyl-Ether	i-Pentane	i-Pentane	Propane	Methyl-cyclo-Hexane
62	s-Butyl-Acetate	Methyl-t-Butyl-Ether	Methyl-t-Butyl-Ether	Methyl-t-Butyl-Ether	Propane
63	Benzene	Acetylene (Ethyne)	Diethyl-Ether	Diethyl-Ether	n-Butyl-Acetate
64	Ethyl-Acetate	i-Propanol	Acetylene (Ethyne)	i-Propanol	Acetylene (Ethyne)
65	i-Propanol	Dimethyl-Ether	s-Butyl-Acetate	Acetylene (Ethyne)	Benzene
66	Acetone	Benzene	i-Propanol	Dimethyl-Ether	Diethyl-Ether
67	i-Pentane	s-Butyl-Acetate	Benzene	s-Butyl-Acetate	Glyoxal
68	Formaldehyde	Acetone	Ethyl-Acetate	Benzene	Dimethyl-Ether
69	Toluene	Ethyl-Acetate	Acetone	Glyoxal	Methanol
70	Ethane	Glyoxal	Glyoxal	Ethyl-Acetate	s-Butyl-Acetate
71	Glyoxal	Ethane	Ethane	Ethane	Ethane
72	Trichloro-Ethene	Methanol	Methanol	Methanol	Acetic Acid
73	Acetic Acid	Acetic Acid	Acetic Acid	Acetic Acid	Ethyl-Acetate
74	Methanol	Trichloro-Ethene	Trichloro-Ethene	Trichloro-Ethene	Trichloro-Ethene
75	1,1-Dichloro-Ethane	1,1-Dichloro-Ethane	1,1-Dichloro-Ethane	1,1-Dichloro-Ethane	Methyl-Acetate
76	Methyl-Acetate	Methyl-Acetate	Methyl-Acetate	Methyl-Acetate	1,1-Dichloro-Ethane
77	Carbon Monoxide	Carbon Monoxide	1,2-Dichloro-Ethane	Carbon Monoxide	Carbon Monoxide
78	1,1-Dichloro-Ethene	1,1-Dichloro-Ethene	Carbon Monoxide	1,1-Dichloro-Ethene	1,1-Dichloro-Ethene
79	Tetrachloro-Ethene	Tetrachloro-Ethene	Benzaldehyde	Tetrachloro-Ethene	Methane
80	Methane	Methane	1,1-Dichloro-Ethene	Methane	Tetrachloro-Ethene
81	1,2-Dichloro-Ethane	1,2-Dichloro-Ethane	Tetrachloro-Ethene	Benzaldehyde	Benzaldehyde
82	1,1,1-Trichloro-Ethane	1,1,1-Trichloro-Ethane	Methane	1,2-Dichloro-Ethane	1,1,1-Trichloro-Ethane
83	Benzaldehyde	Benzaldehyde	1,1,1-Trichloro-Ethane	1,1,1-Trichloro-Ethane	1,2-Dichloro-Ethane