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Sensitivity testing of the model set-up used for calculation of photochemical ozone creation potentials (POCP) under European conditions

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Sammanfattning/Summary

Photochemical Ozone Creation Potentials (POCP) is a method to rank VOC, relative to other VOC, according to their ability to produce ground level ozone. To obtain POCP values valid under European conditions, a critical analysis of the POCP concept has been performed using the IVL photochemical trajectory model.

The critical analysis has concentrated on three VOC (ethene, n-butane and o-xylene) and has analysed the effect on their POCP values when different model parameters were varied. The three species were chosen because of their different degradation mechanisms in the atmosphere and thus their different abilities to produce ozone. The model parameters which have been tested include background emissions, initial concentrations, dry deposition velocities, the features of the added point source and meteorological parameters.

The critical analysis shows that the background emissions of NO_x and VOC have a critical impact on the POCP values. The hour of the day for the point source emission also shows a large influence on the POCP values. Other model parameters which have been studied have not shown such large influence on the POCP values.

Based on the critical analysis a model set-up for calculation of POCP is defined. The variations in POCP values due to changes in the background emissions of NO_x and VOC are so large that they can not be disregarded in the calculation of POCP. It is recommended to calculate POCP ranges based on the extremes in POCP values instead of calculating site specific POCP values. Four individual emission scenarios which produced the extremes in POCP values in the analysis have been selected for future calculation of POCP ranges. The scenarios are constructed based on the emissions in Europe and the resulting POCP ranges are thus intended to be applicable within Europe.

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Foreword

This report is a status report for the IVL jointly funded research program 9.1.1. ’Photochemical oxidant potentials for organic species’.

1. Introduction

Tropospheric ozone

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

In the US, the high concentrations of ground level ozone, which occur in large cities like Los Angeles, cause human health problems. Since traffic is the largest source of emissions, many requirements have therefore 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). The same study shows that 40 % of all children in the school age show symptoms caused by high levels of ozone, such as headache and cough.

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).

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). But the increased background levels of ozone are also a problem since it is proven to cause damage to vegetation (Heck *et al.*, 1988; Skärby *et al.*, 1993; Sandermann *et al.*, 1997). Studies where animals are exposed to ozone show a linear relationship between the exposure to ozone and the amount of biological damage (Lefohn, 1997). Another study which compares the ambient levels of ozone in LA with the number of people admitted to hospital for lung related problems also gives a linear relationship between the concentration of ozone and the number of patients (Wolff, 1996; EPA, 1996). This indicates that there is no threshold concentration below which ozone is not harmful to animals including humans. The EPA in the US has recently decided on new National Ambient Air Quality Standards (NAAQS) for ozone. The previously recommended limit was a 1 hour daily maximum ozone concentration of 120 ppb. This has been reviewed and the EPA has now suggested a new 8 hours limit of 80 ppb which is being debated (Cooney, 1997). In Sweden there have been discussions on whether the recommended ozone concentration limit for health problems should be reduced from the 1 hour daily maximum of 150 ug/cm^3 to 80 ug/cm^3 (Bylin *et al.*, 1996). In the US, the EPA has now also recognised the need for a further ozone limit towards damage to vegetation (Lefohn, 1997). The air quality recommendations for ozone regarding vegetation are all calculated over longer time periods to account for the damage caused by increases in the background levels of ozone. As mentioned above there are indications of ozone being harmful to human health even at lower doses, but these effects are not as well understood as the connection between increased background levels of ozone and damage to vegetation. In Europe the 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·h and is calculated as the sum of the exceedence of ozone above 40 ppb for each daytime hour of the day. Ozone levels below 40 ppb are not included in AOT40. Within the framework of the ECE convention on transboundary air pollution (UNECE LRTAP), critical ozone levels have been worked out by researchers from Europe and North America in a series of workshops. In Europe, where the AOT40 values are used, the critical level for damage to crops has been set to 3000 ppb·h summed over May, June and July, while the corresponding value for forests is set to 10000 ppb·h, calculated over the entire growing season from April until September (Kärenlampi and Skärby, 1996).

The photostationary state

Ground level ozone is formed from nitrogen oxides (NO_x) and volatile organic species (VOC) under the influence of sunlight. The reaction which produces ozone (O_3) in the troposphere is the photolysis of nitrous oxide (NO_2), which produces nitrogen oxide (NO) and atomic oxygen ($O(^3P)$). Atomic oxygen combines with an oxygen molecule (O_2) to form ozone. Ozone can oxidise nitrogen oxide to nitrous oxide and together these reactions form a steady state between ozone, nitrogen oxide and nitrous oxide referred to as the photostationary state (reactions 1-3).

$NO_2 + h\nu \rightarrow NO + O$ (1)
$O + O_2 + M \rightarrow O_3 + M$ (2)
$NO + O_3 \rightarrow NO_2 + O_2$ (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 thereby compete with ozone in the photostationary state. Less ozone is thereby being destroyed through reaction with NO (reaction 3) and hence the ozone concentration increases.

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 and reaction with VOC to form organic nitrate compounds. When NO_x decreases below a certain level the ozone production stops and thus the available amount of NO_x will eventually limit ozone production. The relation between the availability of NO_x and the rate of ozone production is however not linear. At very high concentrations of NO_x the ozone production is in fact inhibited by NO_x through the reaction between NO_2 and OH which is an important radical termination reaction (reaction 4).

$NO_2 + OH \rightarrow HNO_3$ (4)

There are two different states of the atmosphere which are usually referred to as the low and 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 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 densities 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.

Atmospheric chemistry of VOC

Volatile organic compounds are defined as all the organic species which are emitted to the atmosphere in the gas phase. This is a rather loose definition which has no scientific basis but it has turned out to be practical and works in reality. There are many different organic species which falls within the group of VOC and they have different properties. 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, HO_2) (reactions 5 and 6). The reaction which directly affects the ozone concentration is when the peroxy radicals react with NO to form NO_2 (reactions 7 and 9). The organic reaction products from this reaction continues to react in the atmosphere and several peroxy radicals can in this way be produced from one single organic molecule. The main reactions which VOC undergo in the atmosphere are given in reactions 5 - 13 below (Atkinson, 1990).

$RH + OH \rightarrow R + H_2O$ (5)
$R + O_2 + M \rightarrow RO_2 + M$ (6)
$RO_2 + NO \rightarrow RO + NO_2$ (7)
$RO \rightarrow \rightarrow$ carbonyl product(s) + HO_2 (8)
$HO_2 + NO \rightarrow OH + NO_2$ (9)
$RO_2 + NO + M \rightarrow RONO_2 + M$ (10)
$RO_2 + NO_2 + M \rightarrow RO_2NO_2 + M$ (11)
$RO_2 + HO_2 \rightarrow ROOH + O_2$ (12)
$RO_2 + RO_2 \rightarrow$ Products (13)

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).

The increase in ozone, which the presence of VOC causes, depends on the amount of available VOC, the reaction rates for reaction with OH and the concentration of OH and other species, including NO_x, which react with VOC. The concentration of OH is especially important. An organic compound whose reaction path leads to the production of radicals, will enhance the ozone production from all VOC present. If the reaction path instead causes termination of radicals then less ozone will be produced from all VOC. In the high NO_x regime it is principally the above mentioned radical production from the reaction path and the rate constants for reaction with OH which control the ozone production (Dimitriades, 1996; Carter, 1994). When the concentration of VOC becomes to high the ozone production is also inhibited through reactions among peroxy radicals themselves (see reactions 12 and 13 above). This leaves a lower percentage of the peroxy radicals for reactions leading to ozone production, and hence the amount of ozone produced per emitted VOC decreases (Carter, 1994; Bowman and Seinfeld, 1994ab).

VOC is of importance for the ozone production also in low NO_x regime areas, where the formation of ozone is mainly governed by the availability of NO_x. The ability to produce ozone varies between different VOC even under these conditions. Those VOC which through their reaction path leads to a more rapid consumption of NO_x (e.g. through reactions 10 and 11 above), decreases the already low concentration of NO_x. This leads to a lower ozone production not only from that particular VOC but also from all other VOC present. For some VOC this decrease in ozone production, caused by the reduction in NO_x, can more than up-weigh the ozone produced from the actual emission of the specific VOC and hence overall lead to a reduction in ozone. The very same VOC may give a high ozone production under conditions with higher NO_x concentrations (Carter, 1994; Bowman and Seinfeld, 1994ab).

Atmospheric photochemical modelling

Atmospheric photochemical models describe the chemical and meteorological features of the atmosphere and are used to study atmospheric processes. These models are based on kinetic laboratory studies which provide atmospheric reaction mechanisms and reaction rates for NO_x and VOC. Ambient air measurements are needed both for input data and for validation and sensitivity testing of the model output. Emission inventories are also necessary along with meteorological data.

There are mainly two types of models in use within this area, the trajectory models which are one dimensional and describe a box of air as it moves with the speed and direction of the wind over an area, and the Eulerian 3D models which describe the flows of air in and out of a certain volume of air. The 3D models are generally meteorologically detailed while there is not enough computer capacity to handle a complex chemical description. The trajectory models can include a much higher detail of the chemical mechanism but are on the other hand not so capable of describing the meteorological aspects of the atmosphere.

Ranking VOC according to their ability to produce ozone

There is, as outlined above, a need for a tool to compare the ability to produce ozone between different VOC. Several different concepts for VOC ranking have been suggested but they all suffer from certain limitations. Most of these concepts include atmospheric modelling.

Experimental data

Two sets of experimental data is available, k_{OH} reactivity data and incremental reactivities. For both methods, data are derived from experiments performed in smog chambers. Ranking VOC according to their k_{OH} reactivity only gives a comparison on how fast the initial reaction between the hydroxyl radical and different VOC take place. 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). As described previously, the reaction path varies between different VOC. Depending on the number of peroxy radicals which can be produced from a certain VOC, the amount of ozone which can be generated varies. Incremental reactivities (IR) is another method of experimentally estimating the ozone production from different VOC (Carter and Atkinson, 1987; Carter *et al.*, 1995). The method takes into account the reaction path of the VOC and therefore gives a better indication of the ozone which is actually being produced from a certain VOC. The IR of a VOC is defined as the change in ozone caused by the addition of a small amount of that VOC to a scenario, divided by the amount of the VOC that was added. The simultaneous decrease in NO, caused by the direct reaction with ozone, is also included in the measure (Carter and Atkinson, 1989):

$$\mathrm{IR(organic)} = \lim_{\Delta[\mathrm{organic}]\to 0}\left\{\frac{R(\Delta[\mathrm{organic}]) - R(0)}{\Delta[\mathrm{organic}]}\right\} = \frac{\mathrm{d}R}{\mathrm{d[organic]}} \qquad (14)$$

When the change in ozone is calculated, the simultaneous amount of NO which is consumed through the direct reaction between NO and ozone to form NO_2, is also included so that $R(0)$ stands for the maximum of ($[O_3]$ - [NO]) calculated in the base-case simulation, while $R(\Delta[\mathrm{organic}])$ is the maximum of ($[O_3]$ - [NO]) calculated in the simulation with the test VOC added to the base-case. The experimentally determined IR data have been shown to correlate reasonably well with ozone potentials calculated using photochemical grid models (McNair *et al.*, 1992; Carter, 1995). It is however recommended that incremental reactivities, derived through experiments in smog chambers, should not be used directly in regulatory work since the conditions in smog chambers are different from ambient air conditions (Carter and Atkinson, 1989; Carter, 1995).

Many different methods modelling concept have been employed to rank different VOC according to their ability to produce ozone. There is a difference in approach employed in the US and in Europe. In the US, the modelling studies aiming at ranking different VOC are focused on the problem with very high ozone peak values under highly polluted conditions while in Europe, also the ozone production in less polluted areas are considered as well as integrated contributions to the ozone concentrations. The most commonly used methods are incremental reactivities in the US and POCP values in Europe. These concepts will be described more thoroughly below.

Incremental Reactivities (IR-values) from modelling

Incremental reactivities, which as described previously can be derived from experimental data, are also calculated using computer models. The accuracy of the method then depends on how well the atmospheric chemistry of the different VOC are known. The uncertainties in such calculated IR values due to uncertainties in rate coefficients have been estimated to be in between 27 % to 68 %, in a study performed by Yang *et al.* (1995). The same study however concluded that the uncertainties in relative reactivities should be lower than that. The uncertainties in the rate constants for reactions which control the availability of NO_x and radicals are most crucial, but these reactions tend to affect the ozone production from most VOC to the same extent and therefore cancel out to a large extent when relative values are considered (Russel *et al.*, 1995; Yang *et al.*, 1995). The uncertainties in reaction mechanisms and product yields have not been estimated, neither has the uncertainties due to using condensed chemical mechanisms instead of explicit chemical schemes.

Incremental reactivities have shown to vary depending on the conditions under which they are calculated, were the availability of NO_x is an important parameter (Carter and Atkinson, 1987; Carter and Atkinson, 1989). Maximum incremental reactivity (MIR) values are IR values calculated for a scenario were the NO_x level of the base case has been adjusted to give the maximum incremental reactivity of the base case VOC mixture, i.e. where the ozone is most sensitive to VOC. There are also maximum ozone incremental reactivity (MOIR) values which are defined for a base case scenario where the NO_x level has been adjusted to yield the highest peak ozone concentration. In California, MIR values have been applied to develop reactivity adjustment factors (RAFs) which are used to rank different alternative fuels according to their ozone production (CARB 1990; CARB 1991). These reactivity scales which are used in the US are there intended as a compliment to the NO_x control program, implemented in low NO_x areas where the ozone is more sensitive to NO_x than to VOC. Ranking different VOC according to their reactivity in low NO_x areas, has not been considered important in the US since NO_x control is more effective towards ozone in these areas (Croes *et al.*, 1992).

The absolute MIR values have shown to vary significantly between 39 different urban locations in the US. The relative MIR values however showed a much smaller variation with location (Carter, 1994). A comparison between MIR values determined through 1D model simulations and the results from a 3D model has been performed (McNair *et al.*, 1992). The 3D model is run over a longer period of time and therefore makes it possible to compare peak ozone values with ozone exposures. Multi-day effects are important since most ozone episodes lasts several days. During ozone episodes many pollutants are carried over to the following day of the episode causing a build-up of ozone and other oxidants. The study shows that the relative sensitivity of peak ozone and ozone exposure is not identical for all species. The 3D model which was used included a whole range of conditions with a VOC to NO_x ratio of in between 5 and 20. The background conditions, as mentioned previously, affect the ozone production and it is therefore not strange that the ozone formation from a certain VOC varied within the model. The differences in ozone production between the two different types of models used in McNair *et al.,* (1992) are in between 10 % to 20 % for most species. These differences are in the same order of magnitude as some differences in reactivities between different fuel exhausts on which regulatory decisions regarding alternative fuels would be made. Another similar study however, concluded that differences in relative values between peak ozone and ozone integrated over time, shows a relatively small variation between various VOC (Carter, 1994). In a study where MIR values were calculated for two significantly different meteorological situations, the results were similar within an uncertainty of around 10 % (Russel *et al.*, 1995). The same study also included other uncertainty aspects of the MIR concept and concluded that, even when the uncertainties are considered, there are large differences in reactivities between various VOC, which in their opinion justifies the use of reactivities, defined as MIR values, in regulatory decisions (Russel *et al.*, 1995).

Photochemical Ozone Creation Potentials (POCP-values) from modelling

Another method of ranking VOC according to their ability to form ozone is the concept of photochemical ozone creation potentials (POCP), which has been used in Europe (Hough and Derwent, 1987; Derwent and Jenkin, 1991; Andersson-Sköld *et al.*, 1992; Simpson, 1995; Derwent *et al.*, 1996). This method concentrates on larger time scales than the IR method does. The effect from a certain VOC emission is determined by running two separate simulations with the only difference of an extra emission of a certain VOC added to one of them. The amount of ozone which is produced through the additional emission of VOC is then calculated as the difference in ozone 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 (Derwent *et al.*, 1996):

$$\mathrm{POCP}_i = 100 \times \frac{\text{ozone increment with the } i\text{th VOC}}{\text{ozone increment with ethene}} \qquad (15)$$

The POCP value for ethene is hence always equal to 100. POCP values can be calculated both for a specific time along a modelled trajectory, e.g. at maximum ozone concentration, but are often calculated as integrated values over up to 96 hours. The integrated values gives more concern to the effects from long range transport and multi-day photochemistry which is of more importance than the urban scale photooxidant formation in Europe. Depending on how the values are calculated the results vary. The values based on integrated ozone contributions rank more slowly reacting VOC higher than the values based on the increase in ozone at the peak ozone concentration (Andersson-Sköld *et al.*, 1992).

The extra emission of VOC which is added to calculate POCP values can be added as an instant point source to the model (Andersson-Sköld *et al.*, 1992), but also as a steady emission rate along the entire trajectory (Derwent and Jenkin, 1991; Simpson 1991; Derwent *et al.*, 1996). A point source emission describes the effects from an individual unit at a specific site while the constant emissions better describe what would be the case in more general ozone abatement strategy decisions. When the additional VOC is added at a constant emission rate along the trajectory there is a build-up of VOC in the model which is carried over from one day to the other. For species which react fast there will be no carry over of unreacted VOC since there is enough time during one day to break down the additional VOC. For the more slowly reacting species however, there is not enough time for all the extra VOC to react during the day and because of this the amount of VOC builds up within the model from day to day (Derwent and Jenkin, 1991).

The EMEP model has been used to calculate POCP values for European conditions (Simpson, 1991 and 1995). The model divides Europe into over 700 separate squares and runs a trajectory to each and every one of these squares to give a two-dimensional picture of the ozone concentrations in Europe. The growing season of 1985 (April - September) has been used to study how the calculated POCP varies over such a period of time and such a large geographical area. The results given as monthly mean increase in ozone concentrations show large variations in the calculated POCP values which can be attributed mainly to the large differences in both emissions and meteorology in separate parts of Europe (Simpson, 1991 and 1995). There are also large difference in calculated values when the mean values for June are compared with the mean values of April which, besides the other factors presented above, can be explained by differences in temperature.

The effect on POCP values from changing the chemical environment of the trajectories have also been investigated to some extent. The background emissions have been scaled up and down by a factor two which did not give any large differences in the ranking of individual VOC even though the relative POCP values varied somewhat (Derwent and Jenkin, 1991). The study performed using the EMEP model however indicates that there are large differences in POCP values when the full range of emission densities present in Europe is included in the simulations (Simpson, 1991 and 1995). The study by Andersson-Sköld *et al.* (1992) also indicates differences in calculated POCP values as the availability of NO_x is varied.

Derwent and Jenkin (1991) included a comparison with the theoretical number of ozone molecules which can be produced from one molecule of an individual VOC if it goes to complete reaction. This showed, as could be expected, a better agreement between calculated POCP values and theoretical values for the faster reacting species than the slower species. The theoretical ozone potential has been discussed previously when the question of whether the POCP should be calculated as the amount of additional ozone produced, divided by the amount of the added VOC which actually reacted, instead of divided by the amount of VOC which was added regardless of whether it reacted or not (Hough and Derwent, 1987).

Aims of the study

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 and it is therefore desired to work out some sort of generally applicable concept, by which the effects of different emissions could be estimated in various environments, without the need for site specific model simulations.

The aim of this project is to examine the possibility to find a more general way to present POCP values for different VOC under European conditions. In order to do this the robustness of the calculated POCP-values will be analysed towards changes in various model parameters. This process will distinguish any critical parameters which can then be more thoroughly examined. The VOC/NO_x environment is known to be a crucial parameter which highly affects the POCP-values, so this parameter will be given special attention in the study.

One idea which is tested is whether the potential to produce oxidants might be constant for a certain VOC regardless of the chemical environment, and that the availability of VOC and NO_x only determines which reaction paths that are chosen and thus whether ozone or other oxidants are produced. Maybe it would be possible to calculate a total oxidant production which would be less dependant upon the current chemical environment, as well as on other parameters.

VOC which are emitted to the atmosphere react into peroxy radicals as described previously in section about Atmospheric chemistry of VOC. The peroxy radicals can either convert NO to NO_2 or react with other peroxy radicals. Which reaction path which will dominate is largely governed by the amount of available NO_x and VOC. In a chemical scheme, as complicated as the IVL chemical scheme, it will however be much to complicated to try and trace the fate of all peroxy radicals. It is better to try and measure the products from the different reaction paths in some way.

It is the photolysis of NO_2 which generates ozone in the troposphere, but NO_2 can also react in many other ways. Which reactions that take place are, just like previously described for the peroxy radicals, largely dependant on the availability of NO_x and VOC. We have chosen to study the various reaction products of NO_2 (including deposition) to see whether the sum of all these species would be a suitable parameter to describe the total oxidant production from a certain VOC. To get a measure of the total amount of peroxy radicals which initially reacts with NO to produce NO_2, the difference in NO_2 concentration also needs to be considered. If this total sum of NO_2 reaction products and the NO_2 concentration is compared with the sum of reaction products from the reactions among different peroxy radicals, it gives an estimate of which initial reaction path the peroxy radicals have chosen. This comparison can also indicate whether changes in ozone production from a VOC in different VOC/NO_x environments are mainly due to changes in the total production rate of peroxy radicals or an effect of the peroxy radicals choosing other reaction paths.

2. Methods

Model description

The IVL photochemical trajectory 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 have been used in many comparison studies, most recently in the EUROTRAC model intercomparison study (Poppe *et al.*, 1996).

The lower layer of the model describes the boundary layer while the above layer represents the free troposphere. The height of the boundary layer is during the night kept at its minimum value. One hour after sunrise the boundary layer starts to expand, mixing in air from the free troposphere above. The boundary layer reaches its maximum height at 2 p.m. and thereafter stays constant during the rest of the sunlit hours of the day. At sunset, the boundary layer collapses down to its minimum height and at the same time the concentrations of the above layer is set to the concentrations in the boundary layer in the model.

The rate expressions, dC_i/dt, for each species within the model describes the chemical development within each layer of the model. For a species i in the boundary layer, the differential equation which represents the concentration development in time, C_i, will be expressed as in the equation below.

$$\frac{dC_i}{dt} = P_i - L_i C_i - \frac{V_{i,g} C_i}{h} + \frac{E_i}{h} - \frac{(C_i - C_{i,n})}{h} \cdot \frac{dh}{dt}$$

where:

C_i is the concentration of species i in [$molecules \cdot cm^{-3}$] in the boundary layer,
P_i is the chemical production rate in [$molecules \cdot cm^{-3} \cdot s^{-1}$] for species i,
L_i is the chemical loss rate coefficient in [s^{-1}] for species i,
$V_{i,g}$ is the dry deposition rate in [$cm \cdot s^{-1}$] for species i,
h is the height of the mixing layer in [cm],
E_i is the emission rate in [$molecules \cdot cm^{-2} \cdot s^{-1}$] for species i,
$C_{i,n}$ is the concentration of species i in [$molecules \cdot cm^{-3}$] in the air layer above the boundary layer. The second last term, represents the mixing in of air into the boundary layer from the layer above.

For the upper layer, which experiences neither emissions nor dry deposition and which is not affected by any adjacent layer of air, only the first two terms on the right hand side of the continuity equation above, apply.

The differential equations were solved using the calculation program FACSIMILE/CHEKMAT (Curtis and Sweetenham, 1987), employing Gear's method (Gear, 1969) on a Sun Workstation.

Default model set-up

Most of the simulations have been performed using the less detailed chemistry from the EMEP model given in Simpson *et al.*, 1993. This has been done in order to keep down the needed computer time. The EMEP chemical scheme is also an explicit scheme but with much fewer species, in total 70 species taking part in 136 chemical and photochemical 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 (Poppe *et al.*, 1996; Pleijel *et al.*, 1996; Andersson-Sköld and Simpson, 1997). If not otherwise specified the EMEP chemical scheme is used in the simulations.

The study has concentrated on three different VOC to investigate the effects on POCP values when different model parameters are varied. 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. If not otherwise stated all three species have been investigated in all the specified simulation scenarios.

The POCP values are defined as the difference in calculated ozone, or any other measure of oxidant production, between two simulations. The two simulations are one 'reference simulation' and one 'point source simulation' which only differ from the reference simulation in that an extra emissions (a point source) of a certain VOC has been added.

As discussed in the introduction the oxidant production has also been investigated by studying the total change in the various reaction products of NO_2 as well as total change in the reaction products from reactions among peroxy radicals. In the EMEP chemical scheme, NO_2 can end up as PAN and its analogues, HNO_3, N_2O_5 or nitrate; peroxy radicals can produce H_2O_2, ROOH, oxygenates or CO. The changes in all the species mentioned above (including deposition), as a consequence of an extra emission of a certain VOC have been studied for many different scenarios. The concentration of N_2O_5 is taken times two in the sum of NO_2 reaction products since it is formed through the reaction of two NO_2 molecules. In the sum of peroxy radical reaction products the concentrations of both H_2O_2 and ROOH (including deposition) is counted twice since two peroxy radicals are consumed in each reaction. When the IVL chemical scheme has been used the sum of NO_2 reaction products have been limited to include O_3, PAN, HNO_3, N_2O_5 and the deposition of NO_2. The peroxy radical reaction products have been calculated as the sum of H_2O_2, ROOH and aldehydes.

The description of the various model parameters which follow, are all default values which have been used unless otherwise specified.

Meteorology

The production of ozone is highly dependent on the solar irradiance and the highest concentrations of ozone are obtained on days when the solar irradiance is high. The default meteorological parameters are chosen to reflect weather conditions which are favourable for ozone production, i.e. an ozone episode. This is represented by a cloudfree high pressure situation with light winds in the middle of the summer. The diurnal variation of the solar radiation at the 15th of July was used, since it is fairly close to midsummer, when the solar radiation reaches its maximum. The minimum height of the boundary layer is set to 100 m and the maximum height to which it increases is set to 1000 m, which are conditions favourable for ozone production. In the small number of simulations where a single layer have been modelled, the height of the boundary layer has been set to a constant value of 600 m, but unless otherwise specified the height of the boundary layer has been varied as described above. The latitude was chosen to be 58°N which corresponds to Gothenburg in southern Sweden, and the diurnal variations of wind speed, relative humidity and air temperature have been based on around 30 years of weather statistics for southern Sweden (Taesler, 1972). In the model, these parameters are assumed to follow the solar angle during the sunlit hours, whilst during the hours of darkness they are set to constant values. Clouds are in the model assumed to only reduce the solar radiation below them, but this is only of interest when the cloudiness is not equal to zero. The default values for the meteorological parameters used in the simulations are shown in Table 2.1. below.

Table 2.1. The default values for the meteorological parameters used in the model simulations unless otherwise stated. Θ = the solar angle. Sin Θ is set to zero if it is lower than 0.001, i.e. during the night.

Parameter	Default value
Date	15th of July
Latitude	58°N
Boundary layer minimum height	150 [m]
Boundary layer maximum height	1000 [m]
Wind speed	$2 + 1.5 \sin\Theta$ [$m \cdot s^{-1}$]
Temperature	$287.2 + 8.3 \sin\Theta$ [K]
Relative humidity	$78 + 26 \sin\Theta$ [%]
Cloudiness	0/8

Dry deposition

Dry deposition has been included in both chemical schemes. In the EMEP chemical scheme the species O_3, HNO_3, SO_2, NO_2, H_2O_2, PAN and analogues of PAN are deposited. The same species are deposited in the IVL chemical scheme using the same deposition velocities, but the IVL scheme also includes the deposition of aldehydes and organic peroxides. The dry deposition rates are chosen to correspond to the dry deposition over an average Swedish terrain with a 50 % forest coverage. The default values for the dry deposition velocities used in the simulations are given as diurnal mean values in Table 2.2. below.

Table 2.2. Default dry deposition velocities (V_d) used in the model simulations (Pleijel *et al.*, 1992; Simpson *et al.*, 1993).

Species	**V_d** [cm·s^{-1}]
O_3	0.5
HNO_3	2.0
NO_2	0.l5
H_2O_2	0.5
SO_2	0.5
PANs	0.2
Aldehydes	0.3
Organic peroxides	0.5

Emissions

The model includes emissions of NO_x, VOC, CO, SO_2, CH_4 and isoprene. The default values for the emissions which have been used unless otherwise specified are given in Table 2.3. below. The emissions are all based on old emission inventories for Sweden and were used as default values only because they have been applied in several IVL modelling studies in southern Sweden before. As a comparison the emissions for southern Sweden in 1994 are also given in Table 2.3. (except the emissions of CH_4 which are given for 1990). The only emissions which differ significantly are the CH_4 emissions which are overestimated in the default model simulations.

In the EMEP chemical scheme the VOC are emitted as ethane (30 %), n-butane (20 %), ethene (20 %), propene (10 %) and o-xylene (20 %) (Simpson, 1992). In the IVL chemical scheme the VOC are emitted as 77 different VOC including alkanes, alkenes, aromatics, oxygenates and chloroorganic compounds and are distributed as for average Swedish conditions (Janhäll *et al.*, 1995). In Figure 2.1. below a comparison between the distribution of VOC in the two chemical schemes are given. The NO_x emissions are emitted as 95 % NO and 5 % NO_2.

The emissions of NO_x, VOC and CO have been varied over the day according to rush hour traffic. The hours between 7 and 9 in the morning and between 4 and 6 in the afternoon are the busiest traffic hours. Between 9 in the morning and 4 in the afternoon the traffic is not as heavy and during the night there is even less traffic. The distribution of the emissions over the day is given in percentages in Table 2.4. The percentages differ since the share of the emissions which is related to traffic varies from one emission category to another. For VOC half of the emissions come from traffic, while 60 % of the NO_x emissions and 85 % of the CO emissions are related to traffic.

Table 2.3. Default emission densities used in the model simulations and the emissions for southern Sweden in 1994 (EEA, 1995, Janson, 1992; Mylona, 1996; SCB, 1991,1994,1995,1996a, 1996b; Simpson *et al.*, 1995; Skogsstatistisk årsbok, 1993).

Emission category	**Default emission used in the study** [tonnes·km^{-2}·year^{-1}]	**Southern Sweden emissions 1994** [tonnes·km^{-2}·year^{-1}]
NO_x	2.8	2.5
VOC	3.4	2.9
CO	12.4	7.8
SO_2	0.64	0.54
CH_4	21.5	5.1 (for year 1990)
Isoprene	0.50	1.6

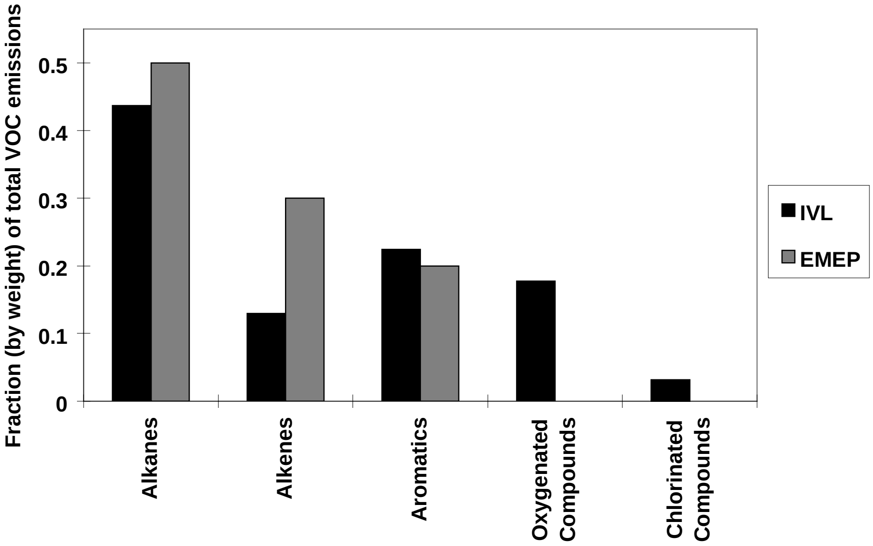

Figure 2.1. The distribution of VOC in different groups of compounds in the IVL and EMEP chemical schemes.

Table 2.4. The diurnal variation of the NO_x, VOC and CO emissions according to rush hour traffic. The percentages differ since different shares of the emissions are related to traffic.

Hours of the day	**% of 24h**	**% of total emission**		
		NO_x	**VOC**	**CO**
7 a.m. - 9 a.m.	8.3	8.8	8.6	9.8
9 a.m. - 4 p.m.	29.2	29.9	29.7	31.6
4 p.m. - 6 p.m.	8.3	8.8	8.6	9.8
6 p.m. - 7 a.m.	54.2	52.5	53.0	48.8

The simulations start at 1 p.m. and the model is run for at least 19 hours before the point source emission is added. This is to make sure that the initial concentrations reflect the current VOC/NO_x environment when the point source is added. The amount of species emitted in the point sources, e.g. from an industrial plant, is given as an emission density per year. If the plume of air which travels along the trajectory is assumed to have a width of 1 km this corresponds to a yearly emission of 100 tonnes for the industrial plant or other kind of individual emission source.

Simulations performed within the study

Initial concentrations

Three different sets of initial concentrations have been tested. These include the definition of an initial concentration of ozone alone, of ozone together with CO and CH_4, and of these three together with NO_x, VOC and some other trace gases (see Table 2.5.). For the case where initial values were defined for VOC and NO_x, the concentrations were obtained from the Swedish TOR station situated at Rörvik on the Swedish west coast. The concentrations represent a polluted air mass which has passed over western Europe before reaching Sweden (Janhäll *et al.*, 1995; Lindskog, 1998). The concentration of ozone was set to 70 ppb which is more than the 50 ppb obtained from the measurements at Rörvik. This was made in order to reflect the generally more polluted European situation (Lindskog, 1997). When defined, the concentration of CO was set to 200 ppb and the concentration of CH_4 was set to 1700, which are values representative for the background concentrations over Europe.

The effect of the initial concentrations were not investigated for the IVL chemical scheme. However, in the other simulations where the IVL chemical scheme were used, the initial concentrations were set according to Table 2.5. below, were the corresponding values used in the EMEP chemical scheme are also given. Notice that the concentration of ozone was set to the measured 50 ppb in the IVL chemical scheme. The initial concentration of CO should have been set to 200 ppb in the IVL chemical scheme, just as in the EMEP chemical scheme, but was unfortunately set to zero due to a programming mistake. The differences in concentration are because the total mass of VOC is preserved between the two chemical schemes as the emissions of a whole range of VOC in the IVL model are converted to the fewer species in the EMEP model.

Table 2.5. Initial concentrations used in the EMEP and IVL model (Janhäll *et al.*, 1995; Lindskog, 1997).

Species	**Initial concentration (ppb)**	
	EMEP	IVL
ozone	70	50
NO_2	4.6	4.6
NO	0.92	0.92
methane	1700	1700
CO	200	-
ethane	1.66	1.27
propane	-	0.43
n-butane	1.65	0.49
i-butane	-	0.28
n-pentane	-	0.16
i-pentane	-	0.29
ethene	0.29	0.29
propene	0.54	0.05
1-butene	-	0.01
2-butene	-	0.01
i-butene	-	0.31
1-pentene	-	0.01
2-pentene	-	0.009
2-methyl-1-butene	-	0.005
2-methyl-2-butene	-	0.006
acetylene	-	0.45
acetaldehyde	0.25	0.25
PAN	0.35	0.35
H_2	500	500
HNO_3	0.1	0.1
H_2O_2	2	2
SO_2	2	2

The point source was emitted at 1 p.m., 24 hours after the start of the simulated trajectories. The point source had an emission density of 1000 tonnes$\cdot$km$^{-2}\cdot$year^{-1} and lasted for 60 s. The scenarios that were simulated are summarised in Table 2.6. below.

Table 2.6. Scenarios simulated to investigate the effect of the initial concentrations.

Scenario	**Initial concentrations given for**
1	O_3
2	O_3, CO, CH_4
3	O_3, CO, CH_4, VOC, NO_x, some other trace gases

Background emissions of SO_2, CO, CH_4 and isoprene

The effect of the background emissions of SO_2, CO, CH_4 and isoprene were tested by varying the emission densities from zero up to a factor 5 times the default values individually for each emission category. The default values were first slightly adjusted to give more even numbers to work around (Table 2.7.). The NO_x emissions were set to 3 tonnes·km^{-2}·year^{-1} and the emissions of VOC were set to 3.5 tonnes·km^{-2}·year^{-1}.

Initial concentrations were given for ozone, CO and CH_4. The point source was emitted at 1 p.m., 24 hours after the start of the simulated trajectories. The point source had an emission density of 1000 tonnes·km^{-2}·year^{-1} and lasted for 60 s. The different emission levels that were simulated are summarised in Table 2.7. below.

Table 2.7. Emission densities, in tonnes·km^{-2}·year^{-1}, used in the simulations investigating the effect of the background emissions of SO_2, CO, CH_4 and isoprene.

Emission category	**Adjusted default emission density**	**Times a factor 0**	**Times a factor 2**	**Times a factor 5**
SO_2	0.5	0	1.0	2.5
CO	12	0	24	60
CH_4	20	0	40	100
Isoprene	0.5	0	1.0	2.5

The shape of the point source emission

The amount of species being emitted in a point source depends on the emission density and on during how long the point source is emitted. These two parameters have been varied while their product has been held constant at 1000 tonnes·km^{-2}·year^{-1} times 60 s.

Initial concentrations were given for ozone, CO and CH_4. The point source was emitted at 1 p.m., 24 hours after the start of the simulated trajectories. The emission density of the point source varied in between 0.7 and 40000 tonnes·km^{-2}·year^{-1} and was emitted during a period of time of in between 1.5 s and 24 hours. The different shapes of the point source are given in Table 2.8. below. The same set of simulation have also been performed, for all three VOC that were tested, but using a single box model with a constant mixing height of 600 m.

Table 2.8. The different shapes of the point source which have been simulated.

Scenario	**Emission density** [tonnes·km^{-2}·year^{-1}]	**Duration of point source in time** [s]
1	0.7	86400 (= 24 h)
2	1	60000
3	10	6000
4	100	600
5	1000	60
6	10000	6
7	20000	3
8	40000	1.5

Hour of the day for the point source emission

The VOC point source has been added at all different hours of the day to see whether this has any effect on the amount of ozone being produced from the point source.

Initial concentrations were given for ozone, CO and CH_4. The point source was emitted in between 12 and 36 hours after the start of the simulated trajectories. The point source had an emission density of 1000 $\text{tonnes}\cdot\text{km}^{-2}\cdot\text{year}^{-1}$ and lasted for 60 s.

The same simulations were run using the IVL chemical scheme. Note that other initial concentrations were used for the these simulations as described in the section about initial concentrations above.

Several sets of simulations using the EMEP chemical scheme have been performed to further investigate the effect of the hour of the day for the emission of a point source. The same set of simulations were used but with slight adjustments.

1. The background emissions were not varied according to rush hour traffic but were held constant throughout the entire simulation. Only ethene was investigated using this set-up.
2. The direct reaction between ethene and ozone was excluded from the chemical scheme. This was also just studied for a point source of ethene.
3. The reaction between formaldehyde (HCHO) and the nitrate radical (NO_3 was excluded from the chemical scheme.
4. The point source was emitted during 1 hour at a decreased density of 16.7 $\text{tonnes}\cdot\text{km}^{-2}\cdot\text{year}^{-1}$.
5. The point source was emitted during 24 hours at a decreased density of 0.7 $\text{tonnes}\cdot\text{km}^{-2}\cdot\text{year}^{-1}$.
6. The deposition of all species were excluded from the chemical scheme.
7. A single box model with a constant mixing height of 600 m was used.

The simulations which were performed are summarised in Table 2.9. below.

Table 2.9. The simulation that have been performed to investigate the effect of changing the time of day for the point source emission.

Model set-up	Chemical scheme	Species added in point source
"Normal"	EMEP	Ethene, n-Butane, o-Xylene
"Normal"	IVL	Ethene, n-Butane, o-Xylene
Constant background emissions	EMEP	Ethene
No reaction between ethene and ozone	EMEP	Ethene
No reaction between HCHO and ozone	EMEP	Ethene, n-Butane, o-Xylene
Point source emitted during 1 hour	EMEP	Ethene, n-Butane, o-Xylene
Point source emitted during 24 hours	EMEP	Ethene
No deposition included	EMEP	Ethene, n-Butane, o-Xylene
Constant mixing height of 600 m	EMEP	Ethene, n-Butane, o-Xylene

The emission density of the VOC point source (tonnes·km^{-2}·year^{-1})

The amount of species which is added in a VOC point source has been varied to conclude within which range the amount of added VOC is large enough to give a measurable difference in ozone and still small enough not to change the VOC/NO$_x$ conditions into which it is emitted.

Initial concentrations were given for ozone, CO and CH$_4$. The point source was emitted at 8 a.m., 19 hours after the start of the simulated trajectories. The emission density of the point source varied in between 0.01 and 107 tonnes·km^{-2}·year^{-1} and was emitted during 60 s. The different point source emission densities that were simulated are summarised in Table 2.10. below.

Table 2.10. The different point source emission densities which have been simulated. The ratio between the point source and the background VOC emission densities are also given.

Scenario	**Point source emission density** [tonnes·km^{-2}·year^{-1}]	**Point source/Background VOC emission density**
1	0.01	$2.96 \cdot 10^{-3}$
2	0.1	$2.96 \cdot 10^{-2}$
3	1	0.296
4	10	2.96
5	100	29.6
6	1000	296
7	10^4	2 960
8	10^5	29 600
9	10^6	296 000
10	10^7	2 960 000

The distribution of the background VOC emissions

The distribution of the background VOC into separate species have been varied to see whether this changes the effect from an added point source. No new species have been introduced so only the relative distribution of the five species which are emitted in the EMEP chemical scheme have been varied.

Initial concentrations were given for ozone, CO and CH$_4$. The point source was emitted at 8 a.m., 19 hours after the start of the simulated trajectories. The point source had an emission density of 1000 tonnes·km^{-2}·year^{-1} and lasted for 60 s.

The different VOC distributions which have been simulated are collected in Table 2.11. below.

Table 2.11. The different background VOC distributions which have been simulated. Simulation number 1 shows the default distribution of the VOC which is used in all other simulations.

Scenario	Fraction by weight of total background VOC				
	Ethane	n-Butane	Ethene	Propene	o-Xylene
1	0.3	0.2	0.2	0.1	0.2
2	0.0	0.286	0.286	0.143	0.286
3	0.375	0.0	0.25	0.125	0.25
4	0.375	0.25	0.0	0.125	0.25
5	0.333	0.222	0.222	0.0	0.222
6	0.375	0.25	0.25	0.125	0.0
7	1.0	0.0	0.0	0.0	0.0
8	0.0	1.0	0.0	0.0	0.0
9	0.0	0.0	1.0	0.0	0.0
10	0.0	0.0	0.0	1.0	0.0
11	0.0	0.0	0.0	0.0	1.0
12	0.5	0.5	0.0	0.0	0.0
13	0.0	0.0	0.5	0.5	0.0
14	0.2	0.2	0.2	0.2	0.2

Initial concentration of ozone

The initial concentration of ozone has been varied to study how this affects the production of ozone from an additional source of VOC emission. Initial concentrations were, besides the concentration of ozone which was varied, given for CO and CH_4.

The point source was emitted during 60 s at 8 a.m., 19 hours after the start of the simulated trajectories.

Two different emission scenarios were investigated. In the first scenario the default emissions were used and the point source emission density was set to 1000 tonnes·km^{-2}·year^{-1}. In the other scenario, which was intended to describe a high-NO_x regime, the VOC emissions were set to 3 tonnes·km^{-2}·year^{-1} and the NO_x emissions to 10 tonnes·km^{-2}·year^{-1} while the point source emission was set to 180 tonnes·km^{-2}·year^{-1}. The background emissions of SO_2 and CH_4 were not altered compared to the default emissions while the emissions of isoprene were set to zero.

For both emission scenarios a range of simulations were performed where the initial concentration of ozone was varied in between 0 and 200 ppb at intervals of 20 ppb, resulting in a total of 11 simulations for each emission scenario.

Dry deposition velocities

The dry deposition velocities have been varied to see whether they influence the amount of ozone which is produced from an additional point source of VOC. All the species which are deposited in the EMEP chemical scheme, i.e. O_3, PAN (including analogues), HNO_3, SO_2, NO_2 and H_2O_2 have been investigated separately.

For ozone and PAN (including analogues), the dry deposition velocities have been varied in between a factor 0 and 2 times their original values and for the other species three different levels have been studied, i.e. their initial values and a factor 0.5 or 1.5 times their original values.

Initial concentrations were given for ozone, CO and CH_4. The point source was emitted at 8 a.m., 19 hours after the start of the simulated trajectories. The point source had an emission density of 1000 $\text{tonnes}\cdot\text{km}^{-2}\cdot\text{year}^{-1}$ and lasted for 60 s.

The different deposition velocities which were simulated are given in Table 2.12. below.

Table 2.12. The dry deposition velocities which have been tested in the simulations. PAN also includes the analogues of PAN. For all simulations only one deposition velocity has been changed at a time. The other velocities are set to the default values.

Factor times default dry deposition velocity	**Dry deposition velocities** [$\text{cm}\cdot\text{s}^{-1}$]					
	O_3	**PAN**	**HNO_3**	**SO_2**	**NO_2**	**H_2O_2**
0	0	0	-	-	-	-
0.1	0.05	0.02	-	-	-	-
0.2	0.10	0.04	-	-	-	-
0.3	0.15	0.06	-	-	-	-
0.4	0.20	0.08	-	-	-	-
0.5	0.25	0.10	1.0	0.25	0.075	0.25
0.6	0.30	0.12	-	-	-	-
0.7	0.35	0.14	-	-	-	-
0.8	0.40	0.16	-	-	-	-
0.9	0.45	0.18	-	-	-	-
1.0 **(Default values)**	**0.5**	**0.2**	**2.0**	**0.5**	**0.15**	**0.5**
1.1	0.55	0.22	-	-	-	-
1.2	0.60	0.24	-	-	-	-
1.3	0.65	0.26	-	-	-	-
1.4	0.70	0.28	-	-	-	-
1.5	0.75	0.30	3.0	1.0	0.225	0.75
1.6	0.80	0.32	-	-	-	-
1.7	0.85	0.34	-	-	-	-
1.8	0.90	0.36	-	-	-	-
1.9	0.95	0.38	-	-	-	-
2.0	1.0	0.4	-	-	-	-

Meteorological parameters

The meteorological parameters which have been investigated are the date, the height of the boundary layer, the temperature, the humidity, the cloudiness and the latitude. The date and the latitude controls the angle of the sun and thus the time of dawn and dusk. The diurnal variation of the temperature and the humidity is controlled by the angle of the sun so the date and the latitude affects these parameters. Since the mixing in to the boundary layer from the top layer is controlled by the time of dawn, the meteorological parameters date and latitude also affects the mixing height during the morning when the mixing in takes place. The cloudiness only affects the calculation of the photolysis rates. Only one meteorological parameter has been varied at a time.

The date affects the mixing in to the boundary layer to a large extent at the default latitude of 58°N. Because of this two different sets of simulations testing the date were performed. In the first the mixing height was controlled by the actual time of dawn in the simulation and in the other the boundary layer conditions were kept as in the default simulation, i.e. the mixing in to the boundary layer was controlled by the time of dawn used in the default simulation. The default values used for the meteorological parameters are summarised in Table 2.13. below.

Initial concentrations were given for ozone, CO and CH_4. The point source was emitted at 8 a.m., 19 hours after the start of the simulated trajectories. The point source had an emission density of 200 tonnes$\cdot$km$^{-2}\cdot$year^{-1} and lasted for 60 s.

Table 2.13. The default values and other values for the meteorological parameters which have been tested. Θ = the solar angle. Sin Θ is set to zero if it is lower than 0.001, i.e. during the night. Only one parameter has been varied at a time while the other parameters have their default values.

Parameter	**Default value**	**Other values which have been tested**
Date	15/7	21/12, 21/1, 21/2, 21/3, 21/4, 21/5, 21/6
Latitude	58°N	40°N, 45°N, 50°N, 55°N, 60°N
Mixing height (min - max)	150 - 1000 [m]	250 - 1000, 150 - 1400
Temperature	287.2 + 8.3·sinΘ [K]	258.3 + 3.5·sinΘ, 277.0 + 9.5·sinΘ, 287.2 + 3.5·sinΘ
Relative humidity	78 + 26·sinΘ [%]	70 + 40·sinΘ, 80 + 35·sinΘ, 90 + 15·sinΘ
Cloudiness	0/8	1/8, 2/8, 4/8, 6/8, 8/8

A first investigation of the VOC/NO_x background emissions

The background emissions of NO_x and VOC have been varied within a large range to assess to what extent the production of ozone from a point source of VOC is affected by changes in the chemical environment into which it is emitted. The background emissions of CO, SO_2, CH_4 and isoprene have not been altered. A total number of 25 scenarios have been simulated. The emission densities of NO_x and VOC have both been varied assuming the values 0.03, 0.3, 3, 30 or 300 tonnes$\cdot$km$^{-2}\cdot$year^{-1} resulting in a 5 by 5 matrix of emission scenarios. The VOC/NO_x ratio was thereby varied in between 0.001 and 1000.

Initial concentrations were given for ozone, CO and CH_4. The point source was emitted at 8 a.m., 19 hours after the start of the simulated trajectories.

Two sets of simulations were performed. In one series of simulations the size of the point source was kept constant throughout all the different scenarios with an emission density of 1000 tonnes·km^{-2}·year^{-1}, and lasted for 60 s. In the other set of simulations the same set-up was used but the amount of VOC emitted in the point source was varied according to the background VOC. The scenario where the background VOC was set to 3 tonnes·km^{-2}·year^{-1} was used as default, setting the point source emission to 1000/3 times the background VOC.

Further analysis of the VOC/NO$_x$ background emissions

The background emissions of NO$_x$ and VOC have been varied within a range of values representing European conditions to study how the chemical environment affects the ozone production due to a VOC point source. The range of emission densities of NO$_x$ and VOC were taken from the EMEP emissions inventory. For each square within the EMEP grid the total amount of NO$_x$ and VOC emissions as well as the ratio of VOC/NO$_x$ were studied separately. Based upon these data the emissions of both NO$_x$ and VOC were set to cover a range from 0.03 up to 30 tonnes·km^{-2}·year^{-1} and the ratio of VOC/NO$_x$ was set to vary between 0.1 and 100. The CO emissions were varied along with the VOC emissions and were set to 3.7 times the VOC which is the ratio between the default emission densities of CO and VOC. As mentioned previously the default emissions are taken from an old emission inventory for Sweden but the resulting ratio of CO/VOC correlates well with the ratio between the total European emission of CO and VOC which was 3.56 for 1994 (Mylona, 1996). A total of 36 different emission scenarios have been tested and they are visualised in Figure 2.2. and Table 2.14. below.

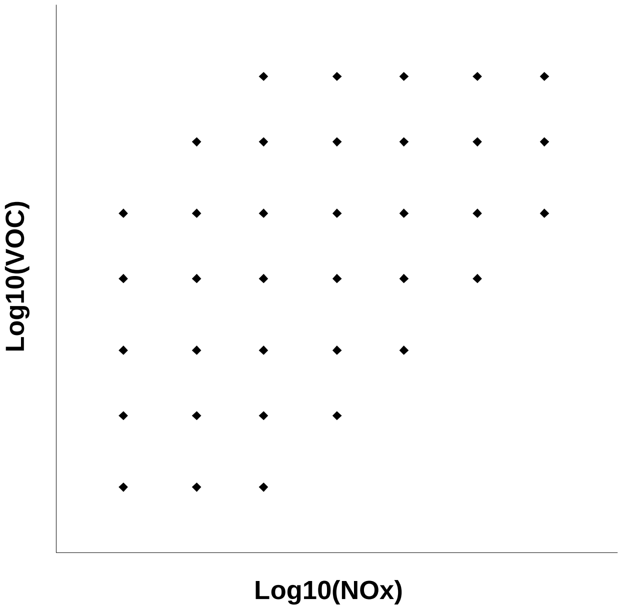

Figure 2.2. The 36 emission scenarios plotted as the logarithm of VOC emission versus the logarithm of NO$_x$ emission. Each point refers to a different emission scenario which has been simulated. There are seven different levels of emission rates for both NO$_x$ and VOC; 0.03, 0.1, 0.3, 1, 3, 10 and 30 tonnes·km^{-2}·year^{-1}.

The point source was emitted during 60 s at 8 a.m., 19 hours after the start of the simulated trajectories. The emission density of the point source was either set to 60 times the background VOC or to a constant emission density of 180 tonnes·km^{-2}·year^{-1} In those scenarios where a point source of NOx was added this was set to 60 times the background emissions of NOx and was emitted as NO and NO_2 with the same ratio between the two species as for the background NO_x emissions. In the scenarios using a point source scaled according to the background the amount of extra VOC or NO_x which is added is the same that is emitted from the background during one hour.

The background emissions of SO_2 and CH_4 have not been altered while the emissions of isoprene have been set to zero.

Initial concentrations were given for ozone, CO and CH_4.

The scenarios were also run using the IVL chemical scheme for a point source of VOC. The only difference between the two sets of simulations, apart from using another chemical scheme, was that the initial concentrations were differently set as described in the section about initial conditions previously.

Table 2.14. The emissions of NO_x and VOC used in the emission scenarios. The simulations have been named after the emission densities of NO_x and VOC. The names start with the letter n (for NO_x emission) followed by a number which indicates the NO_x emission level. This number is followed by the letter v (for VOC emission) which is then followed by another number which gives the VOC emission level. The names for the different levels of emissions are the same for both NO_x and VOC; **level 1** = *0.03 tonnes·km^{-2}·year^{-1}*, **2** = *0.1*, **3** = *0.3*, **4** = *1*, **5** = *3*, **6** = *10*, **7** = *30*.

Name of	**NO_x**	**VOC**	**VOC/NO_x**
scenario	[tonnes·km^{-2}·year^{-1}]		
n1v1	0.03	0.03	1
n1v2	0.03	0.1	3.33
n1v3	0.03	0.3	10
n1v4	0.03	1	33.33
n1v5	0.03	3	100
n2v1	0.1	0.03	0.30
n2v2	0.1	0.1	1
n2v3	0.1	0.3	3
n2v4	0.1	1	10
n2v5	0.1	3	30
n2v6	0.1	10	100
n3v1	0.3	0.03	0.10
n3v2	0.3	0.1	0.33
n3v3	0.3	0.3	1
n3v4	0.3	1	3.33
n3v5	0.3	3	10
n3v6	0.3	10	33.33
n3v7	0.3	30	100
n4v2	1	0.1	0.10
n4v3	1	0.3	0.30
n4v4	1	1	1
n4v5	1	3	3
n4v6	1	10	10
n4v7	1	30	30
n5v3	3	0.3	0.10
n5v4	3	1	0.33
n5v5	3	3	1
n5v6	3	10	3.33
n5v7	3	30	10
n6v4	10	1	0.10
n6v5	10	3	0.30
n6v6	10	10	1
n6v7	10	30	3
n7v5	30	3	0.10
n7v6	30	10	0.33
n7v7	30	30	1

Trajectories with varying VOC/NO_x background emissions

Some simulations where the chemical environment in the trajectory varies with time has been performed. The variations have included extreme changes in both the absolute emissions and the VOC/NO_x ratio. The set-up from the investigation of different VOC/NO_x environments has been used as a basis describing trajectories of a total length of 120 hours (5 days). The trajectories start in one chemical environment which is sustained until 1, 2, 5, 12, 24 or 41 after the point source emission, after which the emissions are changed to reflect another chemical environment.

The emissions of CO have been varied along with the VOC emissions and are set to 3.7 times the background VOC. The background emissions of SO_2 and CH_4 have not been altered, while the emissions of isoprene have been set to 0 throughout all scenarios.

Initial concentrations were given for ozone, CO and CH_4. The point source was emitted during 60 s at 8 a.m., 19 hours after the start of the simulated trajectories. The emission density of the point source was set to 60 times the initial background VOC regardless of the VOC emission density in the second part of the simulation. This way the amount of extra VOC which is added is the same that is emitted from the background during one hour.

For the scenarios where the emissions change at 1, 2, 5, 12 or 24 hours after the point source only ethene and n-butane have been studied (except scenarios n17v5 and n71v5 for which point sources of o-xylene and NO_x have also been tested). For the scenarios where the emissions change first at 41 hours after the point source, all three VOC including also o-xylene have been investigated. The different trajectories which were simulated are given below in Table 2.15.

Table 2.15. Simulated scenarios with varying emissions throughout the trajectory. The simulations have been named after the emission densities of NO_x and VOC which they begin and end in. The n and v in the names stand for NO_x and VOC emissions respectively. The first number after the letter gives the initial emission level and the second number gives the emission level in the second part of the trajectory. If there is no second number it means that these emissions have not been changed from the initial level. The names for the different levels of emissions are the same for both NO_x and VOC; **level 1**= *0.03* $tonnes \cdot km^{-2} \cdot year^{-1}$, **2** = *0.1*, **3** = *0.3*, **4** = *1*, **5** = *3*, **6** = *10*, **7** = *30*. The last column 'Hours after PS' refers to when the change in emissions have taken place, given as hours after the point source. The meaning of 'Only 41' and 'All' is obvious while 'Not 41' means that all cases but the one where the emissions change at 41 hours after the point source, have been run.

Name of scenario	NO_x	VOC	VOC/NO_x	Point source	NO_x	VOC	VOC/NO_x	Hours after PS
	All emissions densities incl. the point source are given in [tonnes·km^{-2}·year^{-1}]							
n12v1	0.03	0.03	1	1.8	0.1	0.03	0.3	Only 41
n1v12	0.03	0.03	1	1.8	0.03	0.1	3.33	"
n12v12	0.03	0.03	1	1.8	0.1	0.1	1	"
n65v6	10	10	1	600	3	10	3.33	"
n6v65	10	10	1	600	10	3	0.3	"
n65v65	10	10	1	600	3	3	1	"
n35v5	0.3	3	10	180	3	3	1	All
n3v57	0.3	3	10	180	0.3	30	100	"
n35v57	0.3	3	10	180	3	30	10	"
n31v4	0.3	1	3.33	60	0.03	1	33.33	"
n3v42	0.3	1	3.33	60	0.3	0.1	0.33	"
n31v42	0.3	1	3.33	60	0.03	0.1	3.33	"
n17v5	0.03	3	100	180	30	3	0.1	Not 41
n71v5	30	3	0.1	180	0.03	3	100	"
n3v17	0.3	0.03	0.1	1.8	0.3	30	100	"
n3v71	0.3	30	100	1800	0.3	0.03	0.1	"
n17v17	0.03	0.03	1	1.8	30	30	1	"
n71v71	30	30	1	1800	0.03	0.03	1	"
n25v63	0.1	10	100	600	3	0.3	0.1	"
n52v36	3	0.3	0.1	18	0.1	10	100	"

Trajectories with varying VOC/NO_x background emissions, but integrated background emissions constant

Simulations have been performed where the emissions vary over the trajectory but the total emissions during the trajectory stays constant. Two different reference cases from the investigation of different VOC/NO_x environments have been used. In the first scenario (referred to as n2v3) the VOC are set to 0.3 and the NO_x to 0.1 tonnes·km^{-2}·year^{-1} and in the second scenario (named n5v5) both the VOC and NO_x are set to 3 tonnes·km^{-2}·year^{-1}. The trajectories which have a total length of 120 hours have been divided into 5 parts of 24 hours each. The emissions have been divided over the different parts at varying emission densities but the total integrated emissions during the entire trajectory has been kept constant. The diurnal variation of the emissions according to rush hour traffic has been employed. Since the different parts are exactly 24 hours long the diurnal variation will not affect the separate parts any differently.

The emissions of CO have been varied along with the VOC emissions and are set to 3.7 times the background VOC and are thus changed if the background VOC emissions are changed. The background emissions of SO_2 and CH_4 have not been altered, while the emissions of isoprene have been set to a constant value of 1.5 tonnes·km^{-2}·year^{-1} throughout all scenarios.

Initial concentrations were given for ozone, CO and CH_4. The point source was emitted during 60 s at 8 a.m., 19 hours after the start of the simulated trajectories. The emission density of the point source was set to 180 tonnes$\cdot$km$^{-2}\cdot$year^{-1}.

Eight different distributions of the emissions over the trajectory have been simulated and for each of these cases NO_x, VOC or both NO_x and VOC have been varied according to the pattern described in Table 2.16. below. This results in 8 times 3 emission scenarios based on each reference case which together with the two reference cases themselves make a total of 50 emission scenarios.

Table 2.16. Distribution of the emissions in simulations where the total integrated emissions over the entire trajectories are kept constant.

Part of the trajectory	**Distribution of emissions in the different cases**							
	Factors taken times the emission density of the reference case.							
	A	**B**	**C**	**D**	**E**	**F**	**G**	**H**
Day 1 (Hours 0 - 24)	2	0.5	5	0	0	4	0	3
Day 2 (Hours 24 - 48)	1	0.5	0	0	0	0.5	0	0
Day 3 (Hours 48 - 72)	1	1	0	5	0	0.5	3	0
Day 4 (Hours 72 - 96)	0.5	1	0	0	0	0	1	1
Day 5 (Hours 96 - 120)	0.5	2	0	0	5	0	1	1

Point source of NO_x

A point source of NO_x has been studied for some scenarios. Two different parameters have been evaluated, the hour of the day for the point source and different VOC/NO_x environments. The ratio between NO and NO_2 in the point source was set to the same as for the background, i.e. 95 % NO and 5 % NO_2.

In the simulations which investigate the effect of adding the point source at different hours of the day the same amount of NO_x, by weight , was added as for a VOC point source.

For studying the effect of a NOx point source in different chemical environments the amount of species emitted was set to 60 times the background NO_x emissions.

3. Results and discussion

Relative and absolute POCP values

POCP values are used to rank different VOC according to their capacity to produce ozone. In many applications a relative measure of the ozone production is more than 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 a Life Cycle Assessment (LCA) where the production of ozone is to be compared with further environmental impacts caused by other pollutants. Relative values are much easier to handle since many of the factors influencing the ozone production cancel out as two simulations using the same set-up are compared with each other. This study has concentrated on the relative POCP values but the impact on the absolute ozone production is also discussed even though not in such great detail as the relative values.

Calculation of POCP

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 responses in 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 response in ozone. Figure 3.1. shows an example of this by comparing the ozone production from ethene, n-butane and o-xylene.

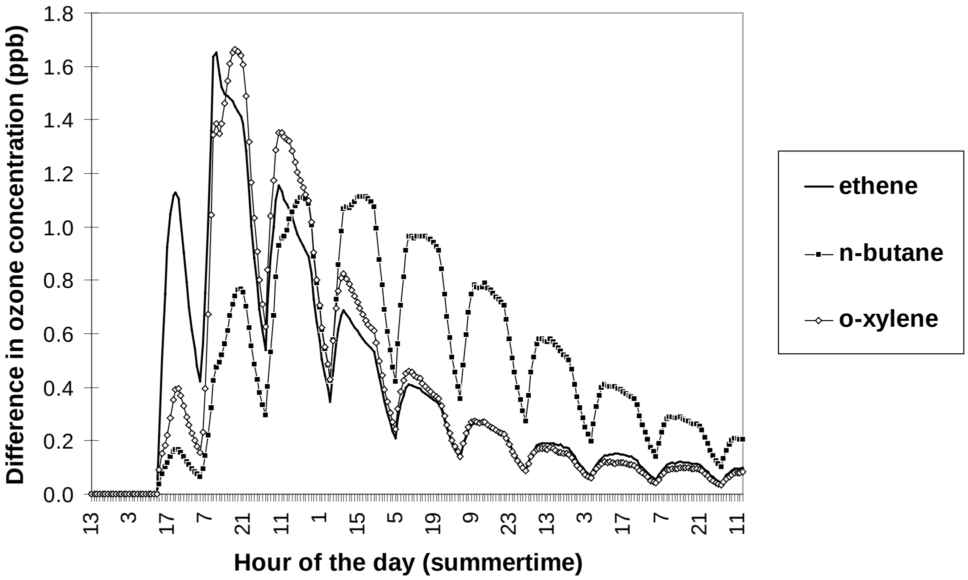

Figure 3.1. The ozone produced from a point source of ethene, n-butane and o-xylene.

Unless otherwise specified, the POCP values in this study have been calculated as average increase in ozone, including deposited ozone, integrated over a time period of 96 hours after the emission of a point source. For the relative POCP values the ozone produced from each VOC is divided by the ozone produced from the same point source of ethene, which gives ethene a POCP value of 1.

The decision to integrate the values over a time period of 96 hours has been based on assumptions regarding meteorological and chemical conditions. The meteorological conditions favourable for ozone production, i.e. the conditions of interest for these sort of calculations, are statistically not stabile for longer than 4 days (Simpson, 1995). After a long time period there is also a probability that the VOC have been removed from the troposphere primarily by dry deposition or precipitation. The trajectory model set-up which has been used does not account for dispersion and thus the box of air which is described by the model should become less realistic after several days. For these reasons we have not calculated the POCP values over a longer time period than 96 hours.

The reason for studying the integrated contribution, instead of the maximum contribution to the ozone concentration from different VOC is that integrated values reflect the health effects as well as the effects on plants, while maximum values mainly relates to health effects. The maximum increase in ozone is however not unimportant and POCP values based on maximum ozone contribution will eventually be calculated along with integrated values as soon as the model set-up, which should be used for POCP calculation, has been decided based on the study.

The robustness of POCP for VOC

Initial concentrations

The amount of ozone which is produced due to a point source of VOC varies with the initial concentrations. The largest contribution to the ozone is obtained when all initial concentrations but ozone are set to zero. The response in ozone is much lower when also CO and CH_4 are given initial concentrations, representative for background troposheric conditions. When NO_x and VOC are present as well, initially, the effect on the ozone production from an extra emission of VOC is again somewhat smaller.

This behaviour is explained by the fact that the extra emission of VOC has the least competition from other VOC in the case where only ozone is defined initially. This means that there are more NO_x available per molecule of VOC in the system and thus the production of ozone per emitted VOC can be more effective (Sillman *et al.*, 1990; Bowman and Seinfeld, 1994b).

The relative POCP values are not affected by whether NO_x and VOC are given initial concentrations or not, as long as CO and CH_4 are present initially. If everything but ozone is set to zero from the start, the ranking of the three VOC changes and the POCP of n-butane becomes higher than the POCP of o-xylene (Figure 3.2.).

Based on these results, initial concentrations are given for ozone, CO and CH_4 in the following simulations.

Background emissions of SO_2, CO, CH_4 and isoprene

The background emissions of isoprene, CH_4 and CO affect the amount of ozone produced from an additional emission of VOC, while the background emissions of SO_2 are of no importance. The isoprene has the largest effect on the ozone production followed by the CO and then the CH_4 emissions. The higher the background emissions of isoprene, CO and CH_4, the lower the contribution to ozone from a point source of VOC. In the cases with higher background emissions there are more VOC available for reaction and therefore the effect of adding additional VOC in a point source is not as significant. Isoprene is the fastest reacting species of the three, and CH_4 the slowest which explains why the emissions of isoprene shows the strongest influence on the resulting ozone concentration and CH_4 the weakest.

The relative POCP values are not affected by the SO_2 emissions and only very slightly affected by the CH_4 emissions. The emissions of CO and isoprene affect the relative POCP values (Figure 3.3.). The ranking of ethene and o-xylene changes as the emissions of CO are set to five times the default emissions.

There are large uncertainties connected with the estimates of biogenic emissions such as isoprene. The results indicate however that the sensitivity of the ozone production towards the level of isoprene emissions is not critical. Based on this the isoprene background emissions were set to the default value of 0.5 $\text{tonnes}\cdot\text{km}^{-2}\cdot\text{year}^{-1}$ in further simulations made in the study. For the same reasons the emissions of CH_4, which are also to a large extent emitted from biogenic sources, were set to the default value of 21.5 $\text{tonnes}\cdot\text{km}^{-2}\cdot\text{year}^{-1}$ in further simulations. Since the emissions of CO are to a large extent emitted by the same processes which give rise to VOC emissions, the CO emissions were set to vary along with the VOC in further simulations. This is believed to be more realistic than to keep the CO emissions constant regardless of the background VOC emissions.

The shape of the point source emission

Species which are emitted to the troposphere can either be highly concentrated as the exhaust from a smoke-stack or more diffuse as leakage from an entire industrial plant. The total amount of species which are emitted may be the same since it takes a longer time for a box of air to pass over an entire industrial plant than just over one chimney and thus the less concentrated emission is maintained for a longer period of time.

The simulations show that for a point source emitted during in between 1.5 s and 10 min there is no difference in the amount of ozone being produced from that point source. When the point source is emitted during longer than 1 hour there is a slight decrease in the production of ozone. The relative POCP values are not affected by the duration in time of the point source if it is 10 min or shorter (Figure 3.4.). For a point source which lasts for 6000 s the ranking of ethene and o-xylene changes.

These simulations were also performed using a single box model which gave no change in ranking of the different VOC. The fact that there is a change in ordering in the scenarios using two boxes may be that the point source is emitted at 1 p.m. and the mixing in to the boundary layer stops at 2 p.m. If the point source lasts for more than one hour which is the case for the scenario in question, this change in the mixing height may be an explanation to the observed change in ranking of ethene and o-xylene

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 ozone being produced from the same source in the late afternoon (Figure 3.5.). The variation in average ozone formation from a point source added at different hours during the night have a rather simple explanation. The effect on integrated ozone is calculated for the 96 hours following the point source. The effect from a point source during the night is however delayed and not seen until the next morning when the sun rises and the photochemistry starts again. The differences in the point sources emitted during the night is thus a result of the contribution during the first hours of the 96 hours being zero for the point sources emitted early during the night. For a point source emitted close before sunrise there is a contribution to the integrated ozone already during the first of the 96 hours.

The relative POCP values varies depending on when the point source is emitted which makes the ordering of ethene and o-xylene change (Figure 3.6.).

There relative POCP values of ethene and n-butane are quite stabile which can be seen in Figure 3.6. This is also shown in the previous Figure 3.5. where the diurnal variation due to the different hour of the day for the point source emission shows the same pattern for ethene and n-butane. The diurnal variation is different for o-xylene which shows an increased ozone production from a point source emitted during the afternoon which can not be seen for the other VOC. This increased production from an afternoon point source is the reason for the change of ordering which takes place between ethene and o-xylene.

The IVL chemical scheme was run to see whether this pattern would repeat itself using a more detailed chemistry. An emission of ethene at different hours of the day was first tested and resulted in the same diurnal variation in the IVL chemical scheme as in the EMEP chemical scheme. The IVL chemical scheme was then also used to simulate emissions of n-butane and o-xylene for almost every hour of the day which indicated the same diurnal pattern as when the EMEP chemical scheme was used. The absolute contribution to ozone was similar for n-butane and o-xylene which was not the case when the EMEP chemistry was used. This leads to similar POCP values for n-butane and o-xylene. The relative POCP values still varies depending on the hour of the day according to the same pattern as previously. The POCP for n-butane and o-xylene however lie closer together and because of this there are changes in the ranking between these species as the hour of the day for the point source varies (Figure 3.7.).

Possible reasons for this diurnal variation was investigated using the EMEP chemical scheme. First the diurnal variations in the background emissions of NO_x, VOC and CO were removed, and a point source of ethene was again investigated. This showed the same diurnal variation in the ozone production as when the background emissions were varied according to rush hour traffic. Since it was ethene that showed the most pronounced diurnal variation of the three VOC, the cause might be related to the reaction mechanism of ethene. One large difference between the reaction mechanisms of ethene and the other two VOC is that ethene decomposition can be initiated via reaction with ozone. The direct reaction between ozone and ethene was therefore removed from the chemical scheme and the different scenarios were run again for a point source of ethene. This resulted in a somewhat higher ozone production and also reduced the amplitude of the variation to some extent, but there was still a very clear diurnal variation. Since more ozone was being produced from a point source emitted during the night and early morning there might be some part of the night chemistry that was responsible for the observed diurnal variation. During the night, the nitrate radical (NO_3) can take over the role of the OH radical and act as an initiator of the VOC oxidation. The only VOC which reacts with NO_3 in the EMEP chemical scheme is formaldehyde (besides isoprene). Ethene also produces more formaldehyde than the other two VOC do. The reaction between HCHO and NO_3 was therefore removed and the different scenarios were run again for all three species. This changed the diurnal variation from a point source of ethene emitted at different hours of the day. The largest amount of ozone was still produced from a point source emitted early in the morning but there was another peak for a point source at 2 p.m. The ozone production was larger for o-xylene than for ethene regardless of the hour of the day for the point source which thus gave o-xylene a higher POCP value (Figure 3.8.).

After discussing the results with Dick Derwent, he suggested that we should let the point source last for 1 hour instead of only 60 s. This however did not change the diurnal variation compared to using a point source of 60 s except that the absolute ozone production from o-xylene was higher than for ethene and as above resulted in a higher POCP value for o-xylene (Figure 3.9.).

When Dick Derwent calculates POCP values he does not add the extra emission as a point source but instead either reduces or increases the emissions of a certain VOC along the entire trajectory. This way of calculating POCP values reflects the effect which changes in the total emissions of Europe would have on the ozone concentration rather than the effect which an individual industrial plant would have on the ozone. Dick Derwent does not see any diurnal variation in his simulations depending on the hour of the day for the point source emission contrary to the results obtained here. The simulations were run again using a point source with the same total emission as before but lasting for 24 hours. The point source emissions were started at different hours of the day but all lasted 24 hours. The integrated response in ozone and ozone deposition over 96 hours was calculated for the 96 hours following the start of the point source emission. This gave no diurnal variation in the amount of ozone produced from the point source. The absolute amount of ozone produced from a point source lasting for 24 hours was much lower than the average ozone production in the cases using a 60 s point source as shown in Figure 3.10.

Ethene does not produce any PAN through its chemical degradation mechanism as both n-butane and o-xylene do. It was suspected that the deposition of PAN and NO_2 might be part of the explanation of the diurnal pattern since the deposition becomes more important during the night in the model. The same deposition velocities are applied but since the height of the mixing layer is much lower during the night the fraction of species which is deposited from the boundary layer is much higher and the concentration thus decreases faster than if a higher mixing height had been used a during the day. The simulations were run without any deposition of any species. There was still a very strong diurnal variation in the amount of ozone produced from a point source and the relative POCP values still varied according to the same pattern, depending on the hour of the day for the point source. The ranking of the three VOC changed as the hour of the day for the point source emission changed in a similar way as in the scenarios when deposition processes were included (Figure 3.11.).

There is a large difference in ozone production between the two 60 s point sources emitted the hour just before and the hour following the time of dusk, compared to the other hours of the day. There is no similar pattern observed around the time of dawn. At dusk there is a sudden drop in the mixing height from its maximum value down to its minimum value. The diurnal variation might therefore be caused by the changes in the mixing height. The scenarios were run again for all three different VOC but using a single box model with a constant mixing height of 600 m. This resulted in a higher total ozone production from the same point source but the diurnal variation of the absolute values remained. The relative POCP values still vary according to the same pattern, depending on the hour of the day for the point source and the ranking of o-xylene and ethene changes for some scenarios (Figure 3.12.).

Since a point source or VOC early in the morning produces more ozone than a point source in the middle of the day, the point source was emitted at 8 a.m. in further simulations in the study.

The emission density of the VOC point source (tonnes·km^{-2}·year^{-1})

When an additional source is added to a scenario it is important to make sure that the chemical environment into which it is emitted is not distorted by it. The point source should be as small as possible and must still be large enough to avoid numerical errors caused by the precision of the calculations.

The emission density of the point source was varied within a large range. For a point source of 10 tonnes·km^{-2}·year^{-1} · 60 s or less, the response in ozone was close to the noise level and was thus affected by numerical errors. In those scenarios where the point source was 100000 tonnes·km^{-2}·year^{-1} · 60 s or larger, which corresponds to around 30000 times the background VOC emission density or more, the OH radical concentration was totally suppressed leading to unrealistic scenario. The point source should therefore be set to a value within the range between these two values. The relative POCP values are given for this range in Figure 3.13. Based on these results the emission density of the point source was set to 60 times the background VOC, which also means that the amount which is emitted in the point source is equal to the amount of VOC emitted from the background during one hour, if the point source lasts for 60 s. Care has to be taken in those scenarios where the VOC background emissions are decreased to make sure that the point source emissions is not decreased to a level where it is affected by numerical errors in the calculations.

The distribution of the background VOC emissions

The distribution of the background VOC affects the total amount of ozone produced from a point source of VOC. More ozone is produced when the background VOC emissions are dominated by slow reacting species since the relative reactivity of the VOC added in the point source is then higher. In the same way, the ozone produced from the point source is decreased if the distribution of the background VOC is shifted towards more reactive species. The relative POCP values also changes with varying distribution of the background VOC (Figure 3.14.). As long as the background VOC are not changed to extreme values such as consisting of only alkanes or only alkenes the effect on the relative POCP is negligible and the default VOC distribution representing an average northern Europe environment has therefore been used in further simulations within the study.

Initial concentration of ozone

The initial concentration of ozone has been varied between zero and 200 ppb in two different emission scenarios. In both individual chemical environments the initial concentration of ozone was shown to influence the total amount of ozone produced from a point source of VOC.

In the default emission scenario the ozone production due to a point source increases as the initial concentration of ozone decreases, giving a maximum production when the initial concentration of ozone is set to zero. The most important source of OH is photolysis of ozone so initially there is no OH radical source in the simulations where ozone is set to zero. As soon as the sun rises there is a production of ozone through the photolysis of NO_2 which is emitted from the background.

In the emission scenario describing a high-NO_x regime the production of ozone from a point source also varies as the initial concentration of ozone changes. The maximum response in ozone is obtained for an initial ozone concentration of around 60 to 80 ppb. The least ozone from a point source emission is produced in the simulation where the initial ozone concentration is set to zero. In this emission scenario there are so much NO_x available that the ozone production is inhibited through the radical termination reaction between OH and NO_2 which produces HNO_3. The maximum response in HNO_3 from a point source also reaches a maximum for an initial ozone concentration of 60 to 80 ppb. As the initial concentration of ozone increases so does the OH radical concentration. In the scenarios with a very low initial ozone concentration the few OH radicals which are produced are quickly consumed through the production of HNO_3 as described above. Since the most important source of OH radicals is the photolysis of ozone, the availability of OH radicals increases as the initial ozone concentration increases. In the scenarios with

In these scenarios there is also an increase in NO_2 when a point source is added, which can be explained by the fact that the point source uses up some of the available OH for reaction and prevents them from producing more HNO_3. If the initial ozone is set to above 20 ppb there is instead a decrease in NO_2 and NO_2 deposition when a point source is added. This is because there is more OH available and thus more

The relative POCP values vary in both emission scenarios as the initial ozone concentration changes (Figure 3.15. and 3.16.). This might be explained by the fact that ethene is more affected by the ozone concentration through the direct reaction between ethene and ozone which the other VOC do not experience. The variation in relative POCP values is not significant in the default emission scenario. In the high-NOx scenario there is a considerable variation in the POCP values with a change of ranking between the different VOC. Within the range of 50 ppb to 130 ppb of ozone, the ranking between the VOC does not change in either of the emission scenarios and the initial concentration of ozone has therefore not been changed from the default value of 70 ppb.

Dry deposition velocities

At first the deposition velocities of all species which are deposited in the model were investigated, i.e. O_3, PAN (including analogues), HNO_3, SO_2, NO_2 and H_2O_2. This showed that it is only the deposition of ozone, PAN and PAN analogues which affect the total ozone production from a point source. The relative POCP values were only affected by changes in the deposition velocities of PAN and analogues (Figure 3.17.). This can be explained since ethene does not produce peroxyacetyl radicals which react with NO_2 to give PAN which is the case for both n-butane and o-xylene.

The deposition velocities of ozone and PAN (incl. analogues) were further investigated based on the obtained results. The amount of total ozone including deposition which is produced from a point source is affected by the ozone deposition velocity. The change in ozone concentration is higher when the deposition velocity is lower, but the opposite is true for the change in deposited ozone which increases along with the deposition velocity. The total change in ozone concentration and amount of deposited ozone is decreased as the deposition velocity of ozone is increased. The relative POCP values are however quite stabile when the ozone deposition velocity is changed, as shown in Figure 3.18.

When the deposition velocity of PAN and its analogues is varied the total production of both ozone and PAN is affected. The production of PAN increase with an increasing deposition velocity while the production of ozone decreases. The pattern is seen for a point source of all three VOC even if it is less pronounced for ethene. This is again explained by the fact that ethene does not give rise to any peroxyacetyl radicals which form PAN through reaction with NO_2. The fact that a point source of ethene still gives an response in PAN is an indirect result from the higher number of NO to NO_2 conversions through reactions with additional RO_2 formed from ethene.

The relative POCP values are slightly affected by changes in the PAN deposition velocity (Figure 3.19.).

Changes in the deposition velocities have not shown to have a critical effect on the relative POCP values and the default deposition velocities have therefore been used throughout the simulations in the study.

Meteorological parameters

Date

The amount of ozone produced from an additional emission of VOC is affected by which date that is simulated. Together with the latitude, the date controls the angle of the sun and thus governs the time of dawn and dusk. The photochemical reactions can only take place during the sunlit hours of the simulations and the time of dawn and dusk therefore has a strong influence on the chemistry which takes place in the simulation. The highest total ozone concentration is obtained in the case where the sunlit part of the day is as long as possible which is on the 21st of June. The angle of the sun also decides the diurnal variation of the temperature and the relative humidity so when the date in the simulation changes, there might be secondary effects due to changes in the temperature and the relative humidity.

The ozone produced from a point source of VOC varies greatly depending on which date that is simulated. Even if the absolute ozone concentration is highest when the day is longest, more ozone is produced from a point source when a shorter day (21st of March) is simulated. This might be explained by the fact that the absolute ozone concentration is lower when the day is shorter, and according to the previous results the amount of ozone produced from a point source increases as the initial ozone concentration decreases. However the day must not be so short that no ozone is produced and this then explains why a maximum is obtained neither for the shortest (21st of December) nor for the longest day which was simulated. This maximum was not seen for a point source of n-butane which gave a maximum contribution to the ozone concentration for the simulation describing the 21st of May. The relative POCP values were greatly affected by which date that was simulated (Figure 3.20.). Since ground level ozone is mainly a summer time problem the winter half of the year is not that important to study and therefore the large variations which are observed as the date is varied within this range need not be considered.

The date affects the mixing in to the boundary layer to a large extent at the default latitude of 58°N. The changes in the mixing height is controlled by the time of dawn and dusk. The mixing in to the boundary layer starts at one hour after dawn and continues until 2 p.m. At dusk the boundary layer is instantly decreased down to its minimum height. The date of the simulation therefore greatly affects the height of the mixing layer and any effects which are seen might be secondary effects due to these changes in the boundary layer. Another set of simulations were therefore performed where the height of the mixing layer was controlled by the time of dawn and dusk of the default date (15th of July) while all other model parameters were set by the dawn and dusk associated with the current date for the simulation. This gave the same results as when the mixing height of the actual date of the simulation was used (Figure 3.21.).

Mixing height of the boundary layer

The height of the boundary layer affects the production of ozone from a point source of VOC. Both the minimum and the maximum mixing height has been varied and it shows that a higher maximum height of the boundary layer produces less ozone. This is simply a result of dilution since a higher mixing height means that the same amount of emissions are released into a larger volume of air, and thus the concentrations become lower. More ozone is however produced if the minimum mixing height is increased, i.e. the height of the boundary layer during the night. This can be explained since the deposition affects the concentrations to a higher extent during the night due to the lower height of the boundary layer. The same absolute amount of species is deposited regardless of the mixing height and thus the relative amount which is deposited is higher if the mixing height is lower. The effect of adding a point source then becomes less in the case using a lower minimum mixing height since more ozone is being removed from the air in this scenario. The relative POCP values varies slightly depending on changes in the mixing height (Figure 3.22.).

Temperature

The temperature varies over the day according to the angle of the sun and reaches a maximum at 1 p.m. Many of the reaction rates and also the water concentration in the air varies with the temperature. The absolute amount of ozone produced from a point source was affected by the temperature. More than twice as much extra ozone was produced from a point source of ethene or o-xylene in the case where a negative temperature was used. This was however not the case for n-butane, which gave most ozone production in the case with the highest temperature. As a consequence of this, the relative POCP values were greatly affected by the choice of temperature but the ordering between the three VOC never changed (Figure 3.23.).

Relative humidity

There is a diurnal variation in the relative humidity which in the same way as for the temperature, is controlled by the angle of the sun. The relative humidity affects the amount of ozone produced from a point source of VOC with less ozone being produced as the humidity increases. The water molecules in the air react with excited O1D radicals from the photolysis of ozone, to produce OH radicals which initiates the oxidation of VOC in the atmosphere. The OH radical concentration is higher in the scenarios where the relative humidity is higher which also leads to a higher concentration of peroxy radicals during the day in these scenarios. If there are more OH radicals available for reaction with VOC, the competition between the VOC molecules decreases and thus the effect of an additional source of VOC is not as important. This is further visualised by the fact that the ozone production due to a point source of n-butane is less affected by changes in the humidity than the two more reactive species ethene and o-xylene are. The relative POCP values are also slightly affected by the changes is humidity (Figure 3.24.).

Cloudiness

The cloudiness controls how much the photolysis rates should be decreased in case of clouds and it is given in eighths where zero refers to clear sky conditions. When the cloudiness is varied from a clear sky to total cloud cover the ozone produced from a point source of VOC varies. For ethene and o-xylene the ozone production increase as the cloudiness increases while for n-butane, the ozone production is instead decreased as the cloudiness increases. The relative POCP values are thus also affected by the cloudiness but for a cloudiness in between zero and two eighths the changes are not critical (Figure 3.25.). Since ground level ozone is mainly a problem when there is little or no cloudiness the large changes in POCP which takes place as the cloudiness moves towards total cloud cover is not a problem which needs to be considered.

Latitude

Changes in the latitude of the simulations only have a minor impact on the amount of ozone produced from a point source of VOC. This might be an effect of the chosen date of the simulations for which the time of dawn and dusk will not change very much depending on the latitude. A range of latitudes in between 40 N and 60 N was tested and the ozone production reached a minimum for a latitude of 45 N for a point source of ethene or o-xylene. For n-butane the least ozone was produced in the scenario using a latitude of 40 N. The relative POCP values are slightly affected when the latitude of the simulations are varied (Figure 3.26.).

For further simulations in the study all the meteorological parameters have been kept at their default values. The mixing height, the relative humidity and the latitude did not have a critical effect on the relative POCP values. For the date, the temperature and the cloudiness there were large variations within some ranges of the tested values. However for the conditions when ground level ozone is considered a problem, the variations were not large enough to justify any changes in the chosen default parameters.

A first investigation of the VOC/NO_x background emissions

The first investigation of the chemical environment was performed using a set of 25 different VOC/NO_x emission scenarios covering a large range of emission densities from 0.03 up to 300 tonnes$\cdot$km$^{-2}\cdot$year^{-1} for both VOC and NO_x and giving a VOC/NO_x ratio in between 0.001 and 1000. Two different series of simulations were carried out, using either a constant point source emission in all scenarios or scaling the point source according to the background emissions of VOC. There are set-backs associated with both of the methods. In the scenarios using an adjusted point source, there were problems with numerical errors in the scenarios experiencing lowest VOC background emissions (0.03 tonnes·km^{-2}·year^{-1}) since the point source was too small. In the cases using a constant point source there will be a drastic change in the chemical environment in the above mentioned low background VOC emission scenarios. Since the point source emission is so much larger than the background VOC emissions in these cases, the chemical environment which was simulated initially is changed towards a scenario with a higher VOC/NO_x ratio.

The absolute production of ozone and other oxidants showed a large variation depending on the chemical environment which can be seen in Figure 3.27. and 3.28., where the average response in NO_2 reaction products is given for the different VOC/NO_x emission scenarios. In Figure 3.27., a constant point source have been added in all scenarios and in Figure 3.28. the point source emission has been scaled according to the background VOC emission.

Up to a certain level, the higher the background emissions of NO_x, the more ozone produced from a point source of VOC. At very high NO_x emissions the ozone production was however lower and there were a significant production of HNO_3. The absolute emissions of NO_x seemed to have a larger effect on the resulting ozone production than the ratio between VOC and NO_x had. The overall pattern of Figure 3.27. and 3.28. is similar except for the scenarios with lowest levels of background VOC emissions. This was at first believed to be due to changes in the chemical environment in the low emission cases when the rather large constant point source had been added. It was however found that the scaled point sources in the lowest VOC emission cases were small enough to be affected by numerical errors.

It was difficult to see any pattern in the production of species resulting from the reactions between peroxyradicals, other than that the production decreased in the scenarios experiencing the highest NO_x emissions. The results showed a need for further simulations without such large distribution, to be able to make out any trends.

The relative POCP values showed large variations depending on the chemical environment which can be seen in Figure 3.29. and 3.30.

The POCP varies depending on the chemical environment which can be seen in Figure 3.29. and 3.30. The values however seem to show a similar pattern regardless of whether the point source emission has been scaled according to the VOC background of if a constant point source emission has been added regardless of the background. The scaled point sources in the lowest VOC emission cases were small enough to be affected by numerical errors and POCP values have therefore not given for these scenarios in Figure 3.30.

Further analysis of the VOC/NO_x background emissions

A further set of 36 simulations describing varying VOC/NO_x environments was performed to investigate the effect on POCP values from different chemical environments more thoroughly. The scenarios included NO_x and VOC emission densities of in between 0.03 up to 30 tonnes·km^{-2}·year^{-1} and VOC/NO_x ratios from

0.1 to 100. The emission scenarios were based on the EMEP emission inventory for Europe and cover the wide range of different environments representative for Europe.

Two separate series of simulations were performed, one using a constant point source emission of 180 tonnes·km^{-2}·year^{-1} and one using a point source scaled according to the background VOC emissions. In the scenarios using an adjusted point source emission the total amount of species emitted in the point source was equal to the amount of VOC emitted from the background during one hour. For the two lowest VOC emission levels (0.03 and 0.1 tonnes·km^{-2}·year^{-1}) the point source was too small and caused problems with numerical errors. The total of seven emission scenarios which this includes have therefore not been evaluated for the simulations using a scaled point source emission.

The absolute production of ozone varies depending on the chemical environment. The amount of ozone produced from a point source of VOC increased with increasing background NO_x emissions. For each individual level of NO_x emissions, the production of ozone due to a point source were larger in those scenarios were the background emissions of VOC were low, i.e. those scenarios with a high VOC/NO_x ratio. For the two highest levels of background NO_x emission there was also a contribution to the HNO_3 production while in the other scenarios the difference in the sum of NO_2 and NO_2 reaction products were totally dominated by ozone and ozone deposition. For the scenarios experiencing the two highest levels of NO_x emissions the results did not show any pattern like the other scenarios did. The overall pattern of the ozone production in the different scenarios is similar for all three VOC which have been tested and the effect of a point source of ethene is given as example in Figure 3.31. and 3.32. The scenarios with a VOC emission density of 0.03 or 0.1 tonnes·km^{-2}·year^{-1} or less is not given for the simulations using an adjusted point source emission since these simulations were affected by numerical errors.

The relative POCP values show a large variation between different chemical environments even if the overall pattern of the absolute ozone production is similar between the three different VOC (Figure 3.33. and 3.34.).

In the scenarios with a VOC emission of 0.03 or 0.1 tonnes·km^{-2}·year^{-1} the point source turned out to be so small that it was affected by the noise level of the calculations, and thus the POCP values for these scenarios are not given in Figure 3.34. For the other scenarios the results are very similar regardless of whether a constant point source has been used or if the point source has been scaled according to the background. This is true for both the absolute response in ozone (Figure 3.31. and 3.32.) and the relative POCP values (Figure 3.33. and 3.34.).

The scenarios which give the most divergent POCP values are those which experience the highest ratio of VOC to NO_x emissions. It is also in these scenarios which some differences can be seen in the absolute ozone production between using a constant point source or a point source scaled according to the background (Figure 3.33. and 3.34.). The POCP values are more stable in the more polluted scenarios and it is also in these scenarios that the most ozone is being produced from an individual point source. It is however difficult to distinguish any pattern in the absolute production of ozone between these scenarios. In the scenarios where the POCP values are fairly stabile the ranking between the three VOC which have been studied is that ethene has the highest POCP value followed by o-xylene and then n-butane.

The absolute change in the sum of products from reactions between peroxy radicals did not change very much depending on the NO_x emissions in the background up to an emission density of 3 tonnes·km^{-2}·year^{-1}. For higher NO_x emissions the absolute changes in peroxy radicals reaction products decreased but as for the changes in NO_2 reaction products the results were difficult to interpret and showed no clear pattern. Within each individual NO_x emission level the absolute change in the sum was lower for the scenarios with higher VOC emissions. The different species within the sum changed as the NO_x emission changed. For the two lowest levels of NO_x emissions the change in H_2O_2 was negative and there was a relatively large response in ROOH. As the background emission of NO_x increases so does the production of H_2O_2 while the production of ROOH decreases (Figure 3.35. and 3.36.). Again, the scenarios with a VOC emission density of 0.03 or 0.1 tonnes·km^{-2}·year^{-1} or less is not given for the scenarios using a point source scaled according to the background since these simulations were affected by numerical errors.

The overall pattern of Figure 3.35. and 3.36. is similar. It is only in the scenarios which have a relatively high VOC/ NO_x ratio that there are noticeable differences in the results between using a constant point source emission and an emission scaled according to the background VOC. These are the same scenarios for which corresponding differences could be seen in the absolute changes in NO_2 and NO_2 reaction products.

The 36 simulations were also run using the IVL chemical scheme, with the point source scaled according to the background VOC in the same way as previously. The response in NO_2 and NO_2 reaction products for these simulations were similar to the results from the EMEP chemistry with some variations for the most highly polluted scenarios. The response from a point source of ethene in different VOC/NO_x environments using the IVL chemical scheme is given in Figure 3.37. The relative POCP values showed larger variations between the scenarios than for the EMEP chemical scheme (Figure 3.38.). As shown previously for the investigation of different hours of the day for the point source there is not such a large difference in ozone production between n-butane and o-xylene when the IVL chemical scheme is used. The POCP values are therefore more similar to each other and there are more changes in the ranking between these two species from one VOC/NO_x scenario to another. The absolute response in the sum of products from reactions between peroxy radicals also changes compared to the EMEP chemical scheme. There are no negative responses in H_2O_2 as there were in the low NO_x scenarios using the EMEP chemistry. For each individual NO_x emission level the response in CO increases as the background VOC emissions increases using the IVL chemical scheme which was not seen for the EMEP chemical scheme (Figure 3.39.).

Trajectories with varying VOC/NO_x background emissions

Trajectories with varying emissions along the trajectory have been calculated for several different VOC/NO_x scenarios. These simulations were run using point source emissions scaled according to the background emissions of VOC and thus some of the results have not been evaluated due to numerical errors in the scenarios with very small point sources. The scenarios include radical changes in emission densities as well as VOC/NO_x ratio.

There were changes both in the absolute production of ozone from a point source, as well as the relative POCP values. Those scenarios which started in an environment limited by the availability of NO_x and proceeded into another limited by VOC, showed a larger production of ozone than any of the constant scenarios. The trajectory which passed through both chemical environments was supplied with both NO_x and VOC and was thus not as strongly limited by any of the precursors as the initial single chemical environment trajectories.

This can be demonstrated by looking at two scenarios which start and end in two different chemical environments, one which is NO_x limited and one which is VOC limited. The two different chemical environments which have been 'mixed' within the trajectories both have a background VOC emission of 3 tonnes$\cdot$km$^{-2}\cdot$year^{-1} but the NO_x background emissions changes from 0.03 tonnes$\cdot$km$^{-2}\cdot$year^{-1} (n1v5, referred to as a low NO_x environment) and 30 tonnes$\cdot$km$^{-2}\cdot$year^{-1} (n7v5, referred to as a high NO_x environment). In Figure 3.40. below the ozone concentration is shown for one trajectory which spends the initial 24 hours in the low NO_x environment and then goes into the high NO_x environment and one trajectory which instead spends the first 24 hours in the high NO_x and then moves into the low NO_x. As a comparison the ozone concentration in the two constant emission scenarios n1v5 and n7v5 are also given. The point source emission is released after 19 hours so the trajectories described above remain in the first chemical environment until 5 hours after the point source emission (19 + 5 = 24) and then changes to the second chemical environment.

The ozone concentration is low in the trajectory which starts in the low NO_x environment since the chemistry is severely limited by NO_x. As the trajectory moves into the high NO_x environment there is initially a sudden increase in ozone concentration but as the high NO_x emissions continue along the trajectory the ozone concentration is suppressed to a low level because of the fast reaction between ozone and NO.

The trajectory which starts in the high NO_x environment also gives a low ozone concentration because of the reaction between ozone and NO. When the trajectory moves into the low NO_x environment the large supply of NO_x ceases and as a result the ozone concentration increases. The ozone concentration at the end of these trajectories which start in the high NO_x and continues into the low NO_x have a higher ozone concentration at the end of the simulations than the two base cases describing either a low or a high NO_x environment.

The trajectory which passes from one chemical environment to another have been performed for several different periods of time. The initial environment has been maintained for 19+1, 19+2, 19+5, 19+12 or 19+24 hours before changing to the other chemical environment. The resulting response in ozone due to a point source in these different trajectories varies. Figures 3.41. and 3.42. show the average response in ozone for a point source of ethene, n-butane, o-xylene or NO_x in the trajectories which either move from a low to a high NO_x environment (Figure 3.41.) or from a high to a low NOx environment (Figure 3.42.).

In all the trajectories which experience both high and low NO_x emissions during the simulation, more ozone is produced from a VOC point source than in either of the two constant chemical environments. This is true regardless of whether the trajectories start in the low or in the high NO_x environment. For a NO_x point source there is an increase in ozone response in the trajectories which start in the low NO_x while there is a decrease in ozone response in the trajectories which start in the high NO_x. The trajectory which gives the highest contribution to ozone from a point source of NO_x is the constant low NO_x scenario which is highly limited by NO_x and therefore gives such a high response.

The chemical environments which are represented in Figures 3.41. and 3.42. are quite extreme but still show some difficulties in trying to interpolate the results from two separate chemical environments into a combination of the two. This is especially true for the relative POCP values which are given in Figure 3.43. for the trajectories described above experiencing both high and low NO_x emissions.

There is no obvious relation between the amount of ozone produced and the emissions experienced in the different trajectories shown in Figure 3.41. and 3.42. Because of this, it is of interest to further investigate the changes in ozone which take place along the different trajectories.

Going from low to high NO_x background emissions

VOC point source

In the trajectories which start in a low NO_x emission scenario and then move into an area with high NO_x emissions, the total amount of ozone produced from a VOC point source depends on the time of day when the higher NO_x emissions are introduced. If the higher NO_x emissions start during daytime the photochemistry is active and the extra NO_x is used to produce ozone. If instead the higher NO_x emissions are introduced during the night the amount of NO_x builds up in the system to such a level that the reaction between ozone and NO effectively suppresses ozone to a lower level. This results in a lower ozone production from the added VOC point source in these scenarios. The lower ozone contribution which is seen in these scenarios can also partly be explained by the fact that the ozone production from the point source is delayed until the day following the night of the higher NO_x emissions. Since the integrated response in ozone is calculated for the 96 hours following the point source emission regardless of the background emissions of NO_x, this results in a lower calculated total ozone production. This is demonstrated in Figure 3.44. where the contribution to ozone for a point source of ethene in the five different trajectories starting in a low NO_x environment and moving into a high NO_x environment is given. The ozone contribution from the point source of ethene is thus higher when the high NO_x environment starts 24 hours after the point source at 8 a.m. the following day, than when the higher NO_x emissions start at 8 p.m. 12 hours after the point source emission of ethene.

NO_x point source

The response in NO_2 and NO_2 reaction products caused by a point source of NO_x is also highly effected by the time of day which the high NO_x environment starts. The later the high NO_x environment starts, the higher the response in ozone from the point source of NO_x (Figure 3.45.) .The importance of the additional point source of NO_x is diminished as soon as the higher NO_x emissions of the background is introduced, reducing the shortage of NO_x. However, the total response in NO_2 and NO_2 reaction products reaches a maximum for the trajectory which stays in the low NO_x environment until 12 hours after the point source (8 p.m.). This is the opposite effect from adding a VOC point source which shows the lowest contribution to NO_2 and NO_2 reaction products of all the scenarios (Figure 3.41.). Again this is explained by the hour of the day for the introduction of the higher NO_x emissions. The ozone concentration, including any extra contribution to ozone caused by an additional point source, is in the model conserved by the layer above the boundary layer during the night. At sunset the concentration of the above layer is set to the concentrations of the lower layer. There are still chemical reactions taking place in this layer but it does not experience any emissions during the night which the boundary layer does. During the morning, air from the above layer mixes into the boundary layer and the height of the boundary layer increases. Thus if the higher NO_x emissions of the background is introduced at 8 p.m., 12 hours after the point source emission, the concentration of ozone during the morning in the boundary layer is much lower than in the above layer since the boundary layer has experienced high NO_x emissions during the entire night. The fact that there is still a large response in ozone from the point source during the second day of this scenario is because the air of the above layer which has conserved the response in ozone is mixed into the boundary layer during the morning (Figure 3.45.). If the high NO_x emissions are introduced in the evening the high NO_x emissions during the night has through the reaction between ozone and NO caused a larger production of NO_2 than in the trajectory where the high NO_x emissions do not start until 8 a.m. 24 hours after the point source. This explains the decrease in the total sum of NO_2 and NO_2 reaction products for the scenario where the high NO_x emissions start 24 hours after the point source (Figure 3.41.).

Going from high to low NO_x background emissions

VOC point source

In the trajectories which move from a high to a low NO_x environment the maximum ozone production from a point source of ethene or o-xylene is obtained when the high NO_x emissions lasts until 1 p.m., 5 hours after the point source emission (Figure 3.42.). For n-butane the response in ozone is the same regardless of whether the low NO_x environment starts at 1, 2 or 5 hours after the point source emission at.

The contribution to ozone from the point source emission is not seen during the first day following the point source since the very high NO_x emissions experienced during the first part of the trajectory is still suppressing the ozone concentration through the reaction between ozone and NO. The maximum response in ozone in each trajectory is reached on the first or second day after the high NO_x emissions have ceased

(Figure 3.46.). For the scenarios where the low NO_x environment does not start until 12 or 24 hours after the point source there is still a large contribution to ozone after 96 hours and the total amount of ozone produced from the point source would have been higher if a longer time period than 96 hours after the point source was considered in the calculations. In the scenarios where the low NO_x emissions start at 1 or 2 hours after the point source there is enough time for the production of ozone to take place but less total NO_x is introduced into the system than in the scenario where the low NO_x emissions start 5 hours after the point source. The combined effect is the seen maximum ozone production for the trajectory where the low NO_x emissions start at 5 hours after the point source.

At a certain point the system changes from being VOC controlled to being NO_x controlled. This can be seen in the total concentration of NO_2 where the concentration comes down to around 1 ppb (Figure 3.47.). At the same time the response in ozone from an additional point source of VOC starts to decrease rapidly. There is even a negative contribution to the ozone concentration from a point source of ethene or o-xylene in the end of the simulations when the NO_2 concentration approaches zero. A point source of n-butane does not give a negative response in ozone production at any time which is demonstrated in Figure 3.48. where the scenario that changes to the low NO_x emissions 5 hours after the point source is given as example. This difference between n-butane and the other VOC may be explained by the differences in atmospheric chemical reaction schemes. The rate of reaction with OH is much lower for n-butane than for the other VOC and n-butane forms PAN which may serve as a storage of NO_2. The lower reaction rate makes n-butane less sensitive to changes in the NO_x background emissions since the OH reaction rate may be limiting the rate of ozone production regardless of the NO_x. The response in ozone from a point source of n-butane is up to five times lower than the response from the other VOC which may explain why less drastic effects are seen from a point source of n-butane.

NO_x point source

When a point source of NO_x is introduced to the trajectories the effect is the opposite from adding a VOC point source. Since the background NO_x emissions are very high at the time of the point source, the extra NO_x emission simply causes a reduction in ozone through the reaction between ozone and NO. As mentioned before the system changes from VOC to NO_x sensitivity at a certain point in each scenario. At the exact same time the negative response in ozone due to the extra point source of NO_x ceases and turns into a positive response in ozone (Figure 3.48.). The largest decrease in ozone is obtained for the trajectory where the low NO_x emissions start at 1p.m., 5 hours after the point source emission. This scenario gave the maximum response in ozone for a VOC point source.

It can be concluded that the changes in emissions in the trajectories which have been studied in detail above, cause a change in the chemical state of the air masses. The scenarios pass between VOC sensitive and NO_x sensitive areas which gives non linear results and makes interpolation of the results difficult. The time of day for the change in chemical environment is of importance since the change from VOC to NO_x sensitivity will behave differently depending on whether daytime or night-time chemistry rules. The effect from adding an additional emission is seen on different time scales depending on the chemical environment and thus the fact that only 96 hours after the point source are being included in the calculations leads to further complications.

Trajectories with varying VOC/NO_x background emissions, but integrated background emissions constant

The results from the scenarios describing trajectories with varying emissions along the trajectory indicated that the total amount of emissions along the trajectory is of importance and not only the individual chemical environments which the trajectory passed through. Two different chemical environments from the previous investigation of different VOC/NO_x scenarios were therefore chosen to simulate different distributions of the emissions along the trajectories. The two different cases that were chosen were one case with rather high emissions referred to as n5v5 and one scenario slightly limited by NO_x, referred to as n2v3. The trajectories with a total length of 120 hours were divided into 5 separate parts of 24 hours each. The emissions were distributed with varying strength over the different parts of the trajectory keeping the total emissions along the trajectory constant between the trajectories (see Table 2.15. in the Methods section of the report).

If only the NO_x or the VOC emissions are changed along the trajectory, the VOC/NO_x ratio also changes compared to the base case scenario. When both the NO_x and the VOC emissions are changed the ratio stays constant and it is only the emission densities which vary between the scenarios.

In Figure 3.49. and 3.50. the response in NO_2 and NO_2 reaction products from a point source of ethene are plotted for the different distributions of emissions for the two base emission scenarios. It is clear from the graphs that in the NO_x limited case (n2v3), variations in the VOC emissions along the trajectory give almost no impact on the response in NO_2 and NO_2 reaction products while changes in the NO_x emissions have a large impact (Figure 3.49.). In the more highly polluted emission case (n5v5) changes in both the NO_x and the VOC emissions have a large impact on the results even though the NO_x emissions seem to be more crucial (Figure 3.50.).

The ozone response is even negative for some scenarios in the NO_x limited scenario (n2v3). For ethene this might be explained by the direct reaction between ethene and ozone which destroys ozone. In a more highly polluted scenario this destruction of ozone would be more than up-weighed by the ozone which is produced from the additional emission of ethene. In the NO_x limited scenario there is not enough NO_x available to produce ozone effectively and compensate for the loss through the reaction between ethene and ozone. For n-butane and o-xylene a negative response in ozone might be explained by the production of PAN and analogues from these species. When PAN is formed the total availability of NO_x in the already NO_x limited system decreases and thus the overall ozone production from all other VOC is inhibited which can result in a negative net effect on ozone.

The resulting POCP values for the two different emission cases and the variations of the emissions along the trajectories are given in Figure 3.51. and 3.52. The POCP values are more stabile in the more highly polluted emission scenario which was also shown previously in the investigation of different VOC/ NO_x environments. The POCP values are unstable and the ranking changes between the three VOC as either of the background emissions are varied. This may to some extent be explained by numerical errors due to the low responses in ozone from a VOC point source, especially for n-butane which gives a much lower response in ozone than the other two VOC. In the more highly polluted scenario, the POCP values are also shown to vary and the ranking between the different VOC changes as the NO_x emissions varies. The changes due to variations in the VOC emissions are not as pronounced and the ordering of the different VOC does not change.

There is a correlation between the amount of emissions during the first part of a trajectory and the response in ozone from an additional point source in that trajectory.

In the more polluted scenario (n5v5) the ozone production is limited by both NO_x and VOC. The effect from changing the background NO_x emissions are however larger than changing the background VOC emissions. The response in ozone due to a point source is affected in the same way when only the NO_x emissions are varied along the trajectories as when both the NO_x and the VOC emissions are varied.

When most of the NO_x are emitted during the first part of the trajectory, the absolute response in ozone from a VOC point source increases compared to the base case, while the response from an additional NO_x point source decreases. The same pattern is observed if only a very small part of the VOC are emitted during the first part of the trajectory.

If instead only a small part of the NO_x are emitted during the first part of trajectory the response in ozone from a VOC point source will decrease and the effect of a NO_x point source will be an increased response in ozone. The same effect is seen if most of the VOC are emitted during the first part of the trajectory.

A point source of n-butane is less sensitive to changes in the background emissions of NO_x. The response in ozone from n-butane stays constant or decreases as the emissions are varied compared to the base case scenario.

In the NO_x limited scenario (n2v3) the effect from changing the background NO_x emissions are more striking than in the other base case scenario.

If most of the NO_x are emitted during the first part of the trajectory the response in ozone will increase substantially compared to the base case. The effect is the same or slightly smaller when both the NO_x and the VOC emissions are varied.

If most of the VOC are emitted in the beginning of the trajectory or if only a small part of the NO_x are emitted during the same part of the trajectory the response in ozone from a VOC point source will increase compared to a uniform distribution of the emissions along the trajectory. The effect is not as large as when the NO_x background emissions or both the NO_x and VOC are varied. The response in ozone from a point source of NO_x is not affected by any changes in the VOC background emissions.

All of the results can be explained by changes in the available amount of NO_x and VOC in the different scenarios. Where and when the transition between the two different chemical states occurs is however very difficult to predict from one case to another. In an air mass which is NO_x sensitive, increased NO_x emissions in the background will increase the possibility to produce ozone from a VOC point source while the ozone produced from a NO_x point source will decrease. An air mass with low VOC background emissions will produce more ozone from a VOC point source because of less competition for the VOC emitted in the point source.

Point source of NO_x

The effect of adding a point source of NO_x has therefore also been investigated for some different scenarios including adding the point source at different hours of the day and looking at different VOC/NO_x environments.

Hour of the day for point source emission

A point source of NO_x was also tested at different hours of the day which gave a very strong diurnal variation which anticorrelated with the variation seen for the VOC point sources (Figure 3.53.). For a NO_x emission during the night the average response in ozone and ozone deposition was negative. This was thought to partly be an effect of how the deposition is handled in the model. The deposition velocities have no diurnal variation in the model but because the mixing height of the boundary layer is decreased during the night, the deposition becomes more efficient since a higher percentage of the species from the boundary layer is deposited.

The simulations were run using the same set-up but without any deposition included. This still gave a very strong diurnal variation but without any negative values as can be seen in Figure 3.54. The variation can thus not be explained by the deposition.

Further analysis of the VOC/NO_x emissions

A point source of NO_x was added in all of the 36 different VOC/NO_x emission scenarios. The amount of NO_x added in the point source was set to 180 $\text{tonnes} \cdot \text{km}^{-2} \cdot \text{year}^{-1}$ or scaled to 60 times the background NO_x emissions. The amount emitted in the scaled point sources thus corresponded to what the background emitted during one hour in the same way as for the VOC point sources scaled according to the background VOC. In the least polluted scenarios there were problems with numerical errors when adding a point source of VOC scaled according to the background VOC. This was however not seen for a point source of NO_x since the sensitivity of ozone towards NO_x was high enough to give a response in ozone well above the noise level. The production of ozone due to a point source of NO_x was highest in those scenarios were the emissions of VOC was lowest. The response increased with increasing background NO_x emissions up to the level of 0.3 $\text{tonnes} \cdot \text{km}^{-2} \cdot \text{year}^{-1}$ after which it decreased again (Figure 3.55. and 3.56.).

The response in ozone and other NO_2 reaction products vary for scenarios with lowest NO_x emissions in the background (Figure 3.55. and 3.56.).The system is most NO_x sensitive in these scenarios and it is not very strange considering the non-linearity of the relationship between NO_x and ozone to see a difference in response because of a difference in the additional NO_x emissions by a factor of 100.

Chapter 3, "Results and discussion", contains references to a number of Figures, also listed in "Table of Figures" at page 50 - 55. However, these Figures are only included in the printed version of the report and not in this electronic version. The printed report is accessible through the IVL office in Stockholm.

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Figure 3.34. POCP values for n-butane and o-xylene, relative to ethene, in scenarios with varying emissions of NO_x and VOC. The point source has been scaled according to the background VOC emissions.

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Figure 3.45. Difference in ozone concentration from a point source of NO_x in different scenarios going from a low NO_x (n1v5) to a high NO_x environment (n7v5). The VOC background emissions have been kept constant at 3 tonnes·km^{-2}·year^{-1} in all scenarios while the NO_x background emissions have varied between 0.03 and 30 tonnes·km^{-2}·year^{-1}. A constant point source of 180 tonnes·km^{-2}·year^{-1} during 60 s has been added in all scenarios.

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Figure 3.50. Average response in NO_2 and NO_2 reaction products over a period of 96 hours after a point source of ethene in different chemical environments where the integrated emissions of both NO_x and VOC along the entire trajectory are 3 tonnes·km^{-2}·year^{-1}. The emissions of

NO_x, VOC or both NO_x and VOC have been varied along the trajectories according to Table 2.15. in the report.

Figure 3.51. POCP values for n-butane, relative to ethene, in different chemical environments where the integrated emissions along the entire trajectory are 0.1 $tonnes \cdot km^{-2} \cdot year^{-1}$ for NO_x and 0.3 $tonnes \cdot km^{-2} \cdot year^{-1}$ for VOC. The emissions of NO_x, VOC or both NO_x and VOC have been varied along the trajectories according to Table 2.15. in the report. A constant point source of 180 $tonnes \cdot km^{-2} \cdot year^{-1}$ during 60 s has been added in all scenarios.

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Figure 3.53. Average response in NO_2 and NO_2 reaction products over a period of 96 hours after a point source of NO_x at different hours of the day.

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Figure 3.56. Average response in NO_2 and NO_2 reaction products over a period of 96 hours after a point source NO_x in different VOC/NO_x emission scenarios. A constant point source of 180 $tonnes \cdot km^{-2} \cdot year^{-1}$ during 60 s has been added in all scenarios.

4. Summary and conclusions

There are different ways to rank the emissions of VOC, according to their ability to produce ground level ozone. One of the methods, the use of POCP values, is evaluated in this study. It can be concluded that although the method is not yet fully applicable as an absolute measure of environmental stress from ozone (to enable a quantitative comparison to other environmental threats), it is still 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 however stays within a certain range which justifies the use of a ranking system instead of treating all VOC as a homogeneous group regarding ozone abatement strategies. 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). Since only three individual VOC species has been studied within the scope of this study, the calculation of POCP values for a larger group of VOC based on the results obtained from this study will be able to confirm (or contradict) this conclusion.

Based on the results from this study, the modelling conditions which should be used for calculating POCP values with the IVL model have been determined. A large number of parameters have been investigated and for many of these parameters, the influence on the absolute amount of ozone which is produced from a point source of VOC is substantial. POCP values are most often calculated relative to a reference VOC, usually ethene. Relative values are generally more stabile 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. Some parameters which have a critical influence on the relative POCP values have been identified by this study. Further calculation of POCP values can thus be optimised to fewer calculations per VOC to fully cover the range of ozone production ability for each individual VOC.

The study has tested the idea that the total oxidant production ability (the sum of ozone, PAN, H_2O_2 etc.) might be constant for a certain VOC regardless of the chemical environment. This would mean that it is the availability of NO_x and VOC which controls the reaction path for the VOC emitted in a point source. As described previously in the introduction there are two main reaction paths for RO_2 radicals, they can either react with to NO give NO_2 or react with other RO_2. The results from this study show that the differences in ozone production is not compensated through production of other oxidants. The sum of NO_2 and NO_2 reaction products is in most environments totally dominated by ozone. In very high NO_x environments other species may dominate the sum or make up a large part of the sum. A low ozone production is not weighed up by reactions between RO_2 radicals. The conclusion is thus that the POCP value is a good relative measure of the oxidant formation from a certain VOC. Including other oxidants in the sum does not make the measure more stabile towards changes in the chemical environment.

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 ozone formation.

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

Modelling conditions for calculating POCP values for VOC

Initial concentrations

The results show that the POCP values did not change as the initial concentrations of VOC and NO_x was set to zero, if only ozone, CO and CH_4 were defined initially. When the background emissions of NO_x and VOC are changed to describe different chemical environments any initial concentrations of VOC and NO_x will be part of the definition of the chemical environment. Since hypothetical air masses have been used in this study it is easier to have only one parameter to define the availability of NO_x and VOC. Based on this, initial concentrations are only be given for ozone, CO and CH_4.

The initial concentrations of CO and CH_4 did not prove to be critical for the relative POCP values. The initial concentration of ozone was not critical in the default emission scenario describing southern Sweden, but for a highly polluted VOC limited scenario the initial ozone concentration had a large effect on the POCP values. Within the range of initial concentrations which are realistic in such a high NO_x scenario however, the ranking of the different VOC did not change. The initial concentration are chosen to represent average European concentrations and the values have been set to 70 ppb for ozone, 200 ppb for CO and 1700 ppb for CH_4.

Background emissions of SO_2, CO, CH_4 and isoprene

The emissions of CO and isoprene did have an impact on the POCP values and the ranking of individual VOC changed for one scenario with very high CO emissions. There are however large uncertainties associated with the emissions of especially isoprene and average European values are chosen since the POCP values are meant to represent the conditions in Europe. The background emissions of SO_2 and CH_4 will be set to 6 and 10 $\text{tonnes}\cdot\text{km}^{-2}\cdot\text{year}^{-1}$ which are average European emissions based on CorinAir 90 (EEA, 1995). The isoprene emissions will be set to 0.26 $\text{tonnes}\cdot\text{km}^{-2}\cdot\text{year}^{-1}$ which reflect average European emissions during growing season (Simpson *et al.*, 1995). The emissions of CO will be varied along with the VOC emissions with a CO/VOC ratio of 3.6 which reflect average European conditions.

The shape of the point source emission

The time of length for the point source has not proven to be critical as long as it is in between 1.5 s and 10 minutes long. The point source will be 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.

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 diurnal variation disappears when the point source is emitted during 24 hours. The results show that the explanation to the observed pattern must lie within the chemistry but no individual reactions have yet been identified as being responsible for the phenomena. The variation can not be explained by variations in the background emissions, the mixing in to the boundary layer from the above layer or the deposition which have all been investigated. The response in ozone from a point source emitted during 24 hours was much lower than the average value calculated from the different values obtained for 60 s point sources at different hours of the day. It is thus not obvious to select the hour of the day which gives the average ozone contribution of the 24 different simulations, in order to simulate a continuous emission source.

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 will therefore be emitted at 8 a.m. in the calculations of POCP values. This is compatible with the decision that non site specific meteorological parameters are chosen to give a maximum production of ozone.

The emission density of the VOC point source (tonnes·km^{-2}·year^{-1})

The emission density of the point source will be set to 180 tonnes·km^{-2}·year^{-1} which is high enough to avoid the noise level and numerical errors associated with it. It is not clear whether the emission scenarios with rather low background emissions will give the correct response for such a point source, or whether the chemical environment changes due to the relatively large point source (compared to the background emissions) so that the response is not representative for the initial chemical environment. It is however a possible scenario for a clean air mass to experience a large point source and this modelling set-up describes such a scenario. Since smaller point sources are associated with numerical errors it is better to use a rather large point source despite the fact that this might change the chemical environment initially described by the modelling set-up.

The distribution of the background VOC emissions

The POCP values were not critically affected by changes in the distribution of the background VOC emissions. Even if all the VOC emissions were emitted in the form of one single species, the ranking of the different VOC did not change. The background VOC will therefore be distributed as average Swedish VOC emissions.

Dry deposition velocities

Changes in the deposition velocities did not have a critical effect on the relative POCP values and the default deposition velocities which are used in the IVL model will therefore be used to calculate POCP values.

Meteorological parameters

The meteorological parameters which have been tested are the date, the mixing height, the temperature, the relative humidity, the cloudiness and the latitude. Out of these, the date, the mixing height of the boundary layer and the temperature have a large influence on the ozone production while the other three parameters do not.

The relative POCP values are not affected by changes in the relative humidity and the latitude and neither by the height of the mixing layer despite the fact that it had a large influence on the absolute ozone production.

For the date, the temperature and the cloudiness, the relative POCP values showed some variation but within the range where ozone formation is generally a problem, the variations were not critical.

Based on these results the meteorological parameters have been set as follows in the calculation of relative POCP values.

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

The mixing height of the boundary layer will be set to 150 m during the night and will then increase up to 1000 m during the morning and mid day hours. The temperature will be set to around 25°C and the relative humidity to around 60 % as average values over the day and both these parameters will 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 will be set to 50°N which corresponds to the central parts of Europe, e.g. the exact latitude for Frankfurt in Germany and Prague in the Czech Republic.

Background emissions of NO_x and VOC

The emissions of NO_x and VOC will be kept constant during the trajectories. The simulations using varying emissions during the trajectories led to very different results especially if the changes in emissions causes a change in NO_x to VOC sensitivity or the other way around. It is difficult to predict whether such a transition will occur in a certain scenario just by looking at the absolute emissions. The time of day, and thus whether daytime or night-time chemistry rules as the changes in emission take place, also affects the results. The variations in POCP values were of the same order of magnitude as the variation between different chemical environments. As described above, other parameters than the actual emissions would affect the POCP values calculated in scenarios with varying background emissions and the results would be more complicated to interpret. In the design of generally applicable POCP values, the use of constant emissions scenarios is thus more useful. These trajectories are hypothetical and are in no way meant to describe a real plume of air passing over Europe. They are however 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 concept to decide whether it is a robust tool to be used in emission reduction strategies.

POCP values will be calculated for four different chemical environments. The four different scenarios: n3v4, n5v4, n5v6 and n6v6, have been selected to include both NO_x limited scenarios and VOC limited scenarios. All emission densities as well as the VOC/NO_x ratio are chosen to be realistic and representative for Europe.

In NO_x limited scenarios, VOC control is not as effective in reducing ozone, but there might be cases where it would be useful to be able to rank individual VOC. We have included a 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 been shown to occur. In many low emission scenarios this limit is not exceeded, and emissions sources which contribute to ozone formation mainly in these areas are therefore not as important to reduce. The low NO_x scenario n3v4 which have $NO_x = 0.3$ tonnes$\cdot$km$^{-2}\cdot$year^{-1} and VOC = 1 tonnes$\cdot$ km$^{-2}\cdot$year^{-1} has a total ozone concentration above 40 ppb and has therefore been chosen. The VOC emissions have been set higher than the NO_x to give a strictly NO_x limited scenario. This emission density is representative for northern Scandinavia.

The scenario n6v6 which have NO_x = VOC = 10 tonnes$\cdot$km$^{-2}\cdot$year^{-1} has been chosen to represent a highly polluted, VOC sensitive emission scenario. This reflects the highest emission densities in Europe on the 150 by 150 km EMEP grid square scale (e.g. Holland and Belgium). The emission densities may locally probably be many times higher than this but that high emissions are not maintained as the air moves over the continent.

In between these two scenarios which represent a low emission scenario and a high emission scenario, two additional scenarios have been chosen. These have been 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 have been chosen are n5v4 and n5v6 with $NO_x = 3$ tonnes$\cdot$km$^{-2}\cdot$year^{-1} and VOC = 1 or 10 tonnes$\cdot$km$^{-2}\cdot$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 densities in Europe. The scenario with the VOC emissions set equal to the NO_x emissions has the same VOC/NO_x ratio as the scenario n6v6 and the POCP values are quite similar.

The initial concentration of ozone had a large influence on the POCP values for the high NO_x scenario which was investigated in this study. It is possible that the initial concentration of ozone will influence the POCP in the VOC/NO_x scenarios which have been selected for further calculations. Limited tests of this sensitivity will be necessary but it is important to remember that a certain scenario is not compatible to any initial concentration of ozone. Large variations in the POCP values are thus only critical if they appear within a realistic range of the initial ozone concentration.

These different environments reflect the varying emission in Europe and covers both NO_x limited and VOC limited scenarios. The scenarios have been selected to cover the range of possible POCP values.

Point source of NO_x

It would be very useful if NO_x could be ranked and be given a POCP value just like individual VOC. The results from the simulations however clearly show the difficulties associated with trying to treat NO_x in the same way as VOC. NO_x works as a catalyst and is not consumed in the ozone production process, in contrast to VOC which is consumed and can be regarded as the fuel in the process. The POCP values are calculated relative another VOC, generally ethene. 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 only have a minor impact. In this system there is not enough catalyst (NO_x) for the system to produce ozone regardless of the amount of available fuel (VOC). 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 which act as the fuel. In the high-NO_x regime the addition of further NO_x will actually reduce the ozone production due to NO titration and the radical termination reaction between NO_2 and OH to form HNO_3, as described in the introduction. Alkenes may react directly with ozone and for these species, e.g. ethene in this study, the effect of adding an additional emission may cause a decrease in ozone in some low-NO_x scenarios. The POCP values for NO_x relative to ethene may thus assume negative values both in high-NO_x regimes where an emission of NO_x gives a reduction in ozone and in some low-NO_x regimes where an emission of ethene causes ozone to decrease. Considering this, POCP values for NO_x may be more confusing than helpful in abatement strategy decision. 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.

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