**TNO Built Environment and Geosciences**

Nederlandse Organisatie voor
toegepast-natuurwetenschappelijk
onderzoek / Netherlands Organisation
for Applied Scientific Research

Laan van Westenenk 501
P.O. Box 342
7300 AH Apeldoorn
The Netherlands

www.tno.nl

P +31 55 549 34 93
F +31 55 541 98 37

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# A consultancy study on volatile organic compounds

## - The POCP-concept in relation to oxygenated solvents -

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Authors D.C. Heslinga *
P.J.H. Builtjes **
M.G.M. Roemer **
A.C. Baart **

* TNO Institute of Environmental and Energy Technology
Department of Air Pollution Control
P.O. Box 342
7300 AH Apeldoorn, The Netherlands

* TNO Institute of Environmental Sciences
Department of Environmental Chemistry
P.O. Box 6011
2600 JA Delft, The Netherlands

Order no. 112326-23429

Intended for Oxygenated Solvents Producers Association
Av. E. van Nieuwenhuyse 4, bte 2
B 1160 Brussels
Belgium
Attention Mr. P. Teheux

## Executive summary

The contribution of Volatile Organic Compound (VOC) emissions to the formation of ozone is accepted to be realistic and VOC emission reduction is part of air pollution regulations under discussion. In this report we discuss the Photochemical Ozone Creation Potential (POCP) concept in relation to these regulations. The report describes the fundamentals and validity of the POCP concept and concludes that it is scientifically sound but that a real validation of the models with respect to ambient ozone measurements is still to be performed. Suggestions for improvement of this situation are being given in the report.

POCP values are given for more than fifty specific solvents, mainly oxygenated solvents, following the Derwent approach, in increasing order. It is discussed that POCP values show an inherent range that finds its origin in the geographical differences in concentrations of precursors and meteorological conditions. Different models show variations in the exact values of the range but these variations are minor to the range itself. However, a ranking of VOC's based on POCP values is possible. For some solvents the uncertainty in POCP value can be reduced by performing model calculations or when better chemical data become available.

To reduce episodic ozone levels a reduction of antropogenic VOC emissions is required. A more pronounced reduction of VOC's with a high POCP value is beneficial and therefore a POCP based emission reduction is to be preferred above a flat rate emission reduction.

It is possible to incorporate POCP values into legislation, existing or being discussed, aiming at VOC emission reduction. No such approach has been enforced in any legislation concerning VOC emissions until now. To do this requires discussion between regulatory, scientific and industrial communities.

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# 1 Introduction

Volatile organic compounds are emitted into the atmosphere by anthropogenic and biogenic sources. By definition, volatile organic compounds, or VOC's, means all organic compounds, other than methane, that are capable of producing photochemical oxidants by reaction with nitrogen oxides in the presence of sunlight (UNECE, 1991). In this definition, next to methane ($CH_4$), also CO is excluded by not being an organic compound.

At a global scale, about 20% of total VOC-emissions is of anthropogenic origin and about 80% of biogenic origin, mainly from forests (see for more information, Roemer, 1991). At a European scale, on a yearly average basis, recent estimates show that about 23% of the VOC-emission will be of natural origin, 34% is due to emissions from transport, 19% comes from solvents, 16% from refineries and chemical industry and 6% from stationary combustion sources (Veldt, 1992).

VOC's play an important role in several aspects of air pollution. On a local scale and at short time scales the direct exposure to toxic, carcinogenic or odorous organic compounds is of concern.

Also VOC-emissions, in combination with $NO_x$-emissions, play a role in the formation of photochemical oxidants. During episodic conditions, elevated concentrations of ozone are formed at local and at large scales. In addition, long-term averaged ozone concentrations at ground level as well as in the free troposphere (2 - 10 km height) are influenced by VOC-emissions, again in combination with $NO_x$-emissions (and to a large extent by CO and $CH_4$-emissions as well). Finally, because during the oxidation of organic compounds CO and $CO_2$ are produced and because VOC's influence the formation of the greenhouse gas ozone, organic compounds also play an - indirect - but relatively small role in the greenhouse effect.

The contribution of antropogenic VOC-emissions to the formation of episodic ozone is of concern to environmental departments of administrations in many countries in the world. Therefore, it is clear that emissions of VOC's will become subject to restrictive legislation more and more in the near future. National initiatives have been undertaken recently, for instance the project 'hydrocarbons 2000' in The Netherlands, or already some time ago, for example the TA-Luft in the Federal Republic of Germany. There is a tendency towards regulation on a larger scale (ECE-UN and European Community) due to the trans boundary character of air pollution and harmonization of national regulations.

Until now no real attention was paid to the incorporation of the potential for ozone formation of different VOC's in legislation. In this report we will present the state-of-the-art of scientific knowledge on this subject.

In this study attention will be restricted to the role of VOC-emissions in photochemical oxidant/ozone formation during episodes, only some remarks will be made with respect to longterm averaged ozone levels.

In chapter two the POCP-concept, its fundamentals and validity will be discussed. In the following chapter the related weaknesses and knowledge gaps of the POCP-approach will be presented, followed by a chapter which gives POCP-values of mainly oxygenated solvents. Chapter 5 discusses the issue of a flat rate or a POCP-based emission reduction, and chapter 6 contains some ideas for POCP-based legislation. In the last chapter conclusions and recommendations are given.

# 2 The POCP-concept, fundamentals and validity

## 2.1 Fundamentals of ozone formation

Photochemical oxidant formation during episodes is a phenomenon which was first observed in the Los Angeles air basin around the beginning of the '50's. In Europe, this phenomenon was observed from the middle of the '60's onwards.

In the principal chemical transformations, $NO_2$ is photolysed first by UV-light to NO and O. Subsequently, O will react with $O_2$ to form $O_3$, and finally $O_3$ reacts with NO back to $NO_2$. From these three reactions the so-called photo-stationary state results:

$$NO + O_3 \rightleftarrows NO_2 + O_2 \qquad (1)$$

Reaction (1) doesn't lead to a net production of ozone. This photo-stationary state can be disturbed to form more ozone by the influence of VOC's, in chemical reactions often presented by RH (Reactive Hydrocarbons, R also stands for groups like $CH_3$, $C_2H_5$ etc). RH reacts with OH and $O_2$ to form $RO_2$ and subsequently $RO_2$ reacts with NO to RO and $NO_2$. In this way NO is transformed to $NO_2$ without the influence of ozone and consequently the equilibrium in reaction (1) will shift to a larger ozone production. The RH-species cover a whole range of different VOC's, with different reaction rates with respect to the OH-radical. So, already from the above given strongly simplified reaction scheme, it is clear that RH-species which react fast with OH will result in a rather fast and high rate of ozone formation. So, RH-reactivity will in principle influence ozone formation.

## 2.2 Aspects of modelling, POCP

### 2.2.1 General

Around 1955, research into the functional relationship between precursor-emissions, $NO_x$ and VOC, and photochemical oxidant formation, mainly focusing on ozone, started with laboratory experiments of the basic chemical reactions. The research continued around 1975 by the development of photochemical oxidant dispersion models. Previous to this more detailed investigations empirical relations were developed between ambient concentrations of VOC and $NO_x$ early in the morning, and maximum ozone concentrations later at that day.

This approach, which is still in use for a first screening exercise - is called Empirical Kinetic Mechanism Approach - EKMA.

Photochemical oxidant dispersion models are based on the dispersion equation of chemical species in the atmosphere. They need as input emission data for $NO_x$ and VOC's; meteorological information like wind speed, turbulence characteristics, mixing height, land use information with respect to dry deposition parameters, and initial and boundary conditions, i.e. concentrations of the relevant species at the beginning of the calculation and at the (mathematical) boundaries of the domain in which calculations are performed. Obviously, there are different types of photochemical oxidant dispersion models. The simplest model is a boxmodel, at a fixed location, covering for example an urban area. Moving boxmodels describe photochemical oxidant formation along a wind-trajectory until a receptor area. In this type of model part of the influence of emissions from outside the area of main interest is taken into account. Finally full three-dimensional models exist, which cover a certain area and take into account differences within that area by dividing that area in relatively small boxes.

Much attention has been given to episodic ozone formation over urban areas over the last 15 years. Next to the research into basic phenomena of ozone formation, attention was given to the calculation of the effect of precursor emission reduction on ozone formation. An excellent overview is given by Seinfeld, 1988.

Seinfeld concludes that full-three dimensional grid based models exist which are appropriate to calculate the relationship between the VOC- and $NO_x$-emissions and the resulting ozone concentration on an urban scale. He also concludes that a combined emission reduction of VOC and $NO_x$ is, in nearly all cases, the best approach to reduce episodic high ozone levels. Seinfeld stresses the point that substantial $NO_x$- and VOC-emission reductions are required to bring maximum ozone levels down.

### 2.2.2 Maximum Incremental Reactivity (MIR)

Even a considerable change in precursor emissions VOC and $NO_x$ leads to relatively small changes in maximum episodic ozone levels (a 'fixed' relationship). As a result, the maximum ozone levels in one of the key non-attainment areas of the US, the Los Angeles Air Basin, hardly have decreased over the last 15 years, despite substantial emission reductions in both VOC- and $NO_x$-emissions, and despite a concept of exempt and non-exempt solvents. Consequently, because ozone levels must be reduced in LA, all feasible counter measures are considered at the moment. Model calculations performed by Carter and Atkinson (1989) showed the possible benefit of a strategy taking into account VOC-reactivity. The reactivity scale introduced in their paper is called Maximum Incremental Reactivity, the MIR-scale. This incremental reactivity is defined in terms of relative changes in ozone formation and NO oxidation caused by the addition of the compound to the total emissions in a series of standard 'scenarios' for representative air pollution episodes.

### 2.2.3 Photochemical Ozone Creation Potential (POCP)

Derwent and Jenkin (1991) developed a similar approach to take the impact of different VOC species into account, the so called photochemical ozone creation potential. POCP is defined as the change in photochemical ozone production due to a change in emission of that particular VOC. In the next paragraph, model results for different types of POCP-approaches will be presented. Here, first some remarks will be made concerning the differences between the MIR-scale and the POCP approach. The remarks are taken from Derwent (April, 1991).

Both approaches are directed to the calculation of the ratio: (change in episodic ozone concentration) / (change in VOC emissions on mass basis).

In the POCP-approach one particular VOC is selected and removed from the emission inventory.
In the POCP-scale this ratio is expressed as an index relative to ethylene = 100. The ozone change at some point in time is therefore first expressed relative to some VOC emission change on a mass basis and then normalised to the same ratio for ethylene.
Consequently, the VOC loading is reduced over the standard model calculation. This results in slightly higher calculated OH-radical concentrations. The impact of removing the VOC is two-fold. First, removing the VOC means that a set of peroxy radical fluxes ($RO_2$, see chapter 2.1) no longer contributes to ozone formation, thereby **reducing** ozone concentrations. Secondly, the increase in OH-concentrations stimulates peroxy radical production from all the VOC's, thereby **increasing** ozone concentrations. For most VOC's, and in most circumstances, taking away VOC's leads to slightly lower ozone concentrations, but not necessarily.

Both the MIR-scale and the POCP-approach address the ability of each VOC to compete for OH-radicals and the ability of the fragments formed following OH attack, to produce ozone.
The two scales are basically identical.
However, the POCP-approach and the MIR-scale are chemical mechanism dependent, and they vary with the environment to which they are applied. The MIR-scale is applied to the LA-air basin. The POCP-approach is directed to Europe. These are indeed markedly different areas, for example the OH-concentration over Europe appears to be higher because $NO_x$-levels are lower.
Differences between the MIR-scale and the POCP-approach can be fully explained by the differences mentioned, but again they are basically identical.

### 2.2.4 Emission abatement: MIR

It is worthwhile to mention some aspects of the MIR-approach as it is currently used in California. A conference was held on April 8 and 9, 1991 in Irvine, California, entitled 'Reactivity-Based Hydrocarbon Controls: Scientific Issues and Potential Regulatory Applications' sponsored by the California Air Resources Board and the South Coast Air Quality Management District. The main aim of the conference was a review by the scientific community of the California Air Resources Board proposal to use the MIR-scale in developing an optimal ozone abatement strategy, or to produce a 'better' set of data that is more defensible than the MIR-scale. Generally speaking the review showed that a reactivity scale like the MIR-scale is feasible, but that the ranges of the values in the scale might be considerable (see for example Whitten, 1991). This point will be addressed further in chapter 3 of this report.

With respect to the abatement strategies which are planned in California using the MIR-scale, it is interesting to note that the issue is solely focused at the moment on traffic-exhaust. Plans are under development of a protocol on ozone reactivity scale for low-emission vehicles and clean fuels. (Croes and Carter, 1991). Until now, as far as written information concerning the abatement strategy plans in California is available, the possibility of using the MIR-scale in relation to solvents emissions is not mentioned. This might be due to the already strict regulations with respect to the use of solvents in California.

### 2.2.5 Emission abatement: POCP

In 1990 and 1991, in the framework of the UNECE convention on long range transboundary air pollution the policy was being formulated to reduce the emissions of volatile organic compounds, VOC's, following the already formulated policy with respect tot $SO_x$- and $NO_x$-emission.
The concept of the POCP-approach was brought into discussion as a guidance to improve the effectivity of abatement strategies of VOC-emissions.
The concept of the POCP approach (and the MIR-scale) resembles strongly the concept of Ozone Depletion Potential, ODP as it is used in the abatement strategies with respect to the protection of the stratospheric ozone layer, and the concept of Global Warning Potential, GWP, as it is used in the policy development to abate the increased greenhouse effects.
In all three situations, the different concepts are directed to the determination of an adequate and optimal **ranking** of the trace gasses involved, to enable a policy in which the 'worst' trace gasses are abated first. Also in all three concepts there is a possibility to quantify the effect of replacing a 'bad' trace gas with a 'not so bad' trace gas, in case the complete reduction of the 'bad' and 'not so bad' tracegas is, for several reasons, impossible or very hard to achieve.

The final UNECE protocol concerning the control of emissions of volatile organic compounds or their transboundary fluxes, as it has been formulated at the ninth session November 18 - 22, 1991 in Geneva, aims, in general terms, at a reduction of VOC-emissions per country of at least 30% in 1999, using 1988 levels as a basis (or another year between 1984 to 1990). This VOC-emission reduction is strictly on a mass basis. Attached to the protocol is a technical annex, annex IV entitled 'Classification of VOC's based on their photochemical ozone creation potential (POCP). The technical annex is meant to provide guidance on control policies for VOC's, taking into account the impact of each VOC species expressed in terms of the POCP-approach. The text of this annex is presented in Appendix A of this report.

It should be emphasised here, that the POCP-ranking which is presented as guidance in the technical annex to the protocol does not take the mass of a VOC-specie itself explicit into account. The ranking is strictly on a POCP-basis. However, it should be clear that × kg of a VOC-specie which has a POCP-value of 50 'produces' the same amount of ozone molecules as 5 × kg of a VOC-specie with a POCP-value of 10. A final and detailed legislation should adress this item in its full extent.

During the drafting of this annex, several types of POCP calculations have been performed, using the Harwell trajectory model, the Swedish point source model, the EMEP model and the LOTOS model.

## The Harwell trajectory model

The first, and with respect to the amount of VOC species considered, most extensive calculations are performed by Derwent and Jenkin, (1991).
The calculations are performed in the following way. Model calculations have been carried out using the Harwell trajectory model. A detailed chemical mechanism has been used involving 384 chemical species and 684 chemical reactions. Trajectories across the Southern British Isles (1 day), from the Federal Republic of Germany to the Republic of Ireland (5 day trajectory) and from France to Sweden (5 day trajectory) have been studied.

The POCP values have been determined for each day, at mid afternoon, leaving out the first day of the 5 day trajectory cases, so in total 9 days over 3 situations. Both the averaged POCP-value over the 9 days, and the range over all (11 days) has been determined, see Table 3 of the annex (Appendix A).

It should be mentioned that the detailed ranking of VOC-species using the POCP-values of the first day differs from the ranking using the POCP-values of the fifth day. The latter should be considered as more realistic because normally photochemical episodes over Europe last for a couple of days, say between 3 - 6 days.

## The Swedish point source and the EMEP model

A different POCP-concept has been elaborated by Andersson - Sköld e.a., 1991. This Swedish approach considers the impact of an isolated point source of each hydrocarbon in background air appropriate to southern Scandinavia which means under low $NO_x$-concentration. Calculated are the maximum differences in ozone concentration, with and without the hydrocarbon emission, anywhere downwind of the source. Calculations have been performed for 1 day, and over 4 days. Again results are presented in Table 3 of the annex.
The approach of Derwent gives results for the north-western part of Europe, the Swedish approach is only valid for southern Scandinavia. To obtain information concerning the POCP-value over total Europe, model calculations are performed with the EMEP-trajectory model and with the Eulerian grid model LOTOS (long term ozone simulation).
The EMEP-trajectory model is a single layer trajectory model which calculates concentrations of photochemical oxidants every 6 hours for the 709 receptor grids (150 × 150 $km^2$) over Europe. Model calculations have been performed for July 1985. The EMEP-emissions are only presented by six species, ethane, ethylene, n-butane, o-xylene and ethanol. Consequently, POCP-values can only be calculated for these six species. However, the model makes it possible to calculate POCP-values for these species over the whole of Europe. Again the results of the calculation is presented in Table 3 of the annex. The results are presented as the range of 5 - 95 percentile over the whole area. This range over Europe is caused by the different $NO_x$- and VOC-emissions per grid, and the different influences of

grids on each other due to the specific meteorological conditions. As an example in Figure 1, the EMEP-POCP value for n-butane is presented, for ozone levels above 60 ppb (see for more information, Simpson, January 1991).

## The LOTOS model

Finally, POCP -calculations have been performed with the LOTOS-model. The LOTOS-emission data base contains per source category next to the amount of VOC-emissions in kg, a VOC-speciation which is different for each source category and - if information is available - different for each country. As an example, in the next table the VOC-speciation for solvents is given (Veldt, 1985).

*Table 1 VOC-speciation for solvents, on a mass-basis in LOTOS*

| Species | Percentage % |
|---|---|
| Alkanes, > C4 | 32 |
| Toluene | 6 |
| Xylene | 4 |
| Aromatics > C10 | 5 |
| Methanol | 2 |
| Ethanol | 6 |
| Acetone | 4 |
| Methyl ethyl ketone (MEK) | 3 |
| Methyl isobutyl ketone | 2 |
| Isopropyl alcohol | 5 |
| Other alcohols | 3 |
| Trichloroethylene | 3 |
| Methyl chloride | 5 |
| Ethers | 2 |
| Acetates | 7 |
| Perchloroethylene | 4 |
| Other chlorinated solvents | 3 |
| Chlorofluorocarbons | 4 |

It should be noted that by lack of information this speciation holds for the total source category 'solvents', and is used for every European country, western and eastern Europe.

With the LOTOS-model and its input, POCP values can be calculated in principle for every VOC-species. The model calculations are performed for July 1985, with a grid resolution over Europe of 1° latitude × 2° longitude (35 × 35 grids). POCP results are presented for the ozone differences for July 15, 1985 15.00 pm with the emission reduction per VOC-species starting by July 1. For details concerning the performed calculations, see Builtjes, April 1991. Also here, as an example in

Figure 2 the LOTOS-POCP values for n-butane are given. In Figure 2 the number -99 means an invalid result due to mathematical insignificant differences in ozone concentrations. It is clear from Figure 2 that the POCP range calculated by LOTOS is even larger than for EMEP. Again, the 20 - 80 percentile LOTOS-results are given in Table 3 of the annex.

### 2.2.6 Conclusions

A few questions arise when considering the different model calculations. First, a remark should be made concerning the POCP-values for 1 day, 5 days, or 14 days (as has been performed with LOTOS). As has been stated already, realistic POCP-values should be the values obtained after calculations of a couple of days. Analysis of the LOTOS-results for POCP on different days, and the results by Simpson (June, 1991), for a calculation of over one month show that the POCP-ranking does not change anymore for calculations which are larger than a couple of days (although absolute POCP-values can be different).
This rather surprising result might be due to the choice of ethylene as the basis for the calculations. Because ethylene is rather reactive - not many VOC-species have a POCP above 100, which is taken as the reference for ethylene, - calculations which cover more than a couple of days are already ‘long’ relative to ethylene. Consequently, calculations which cover a couple of days will not be different from calculations which cover 14 days, or a month, or even a year. With respect to a full evaluation of POCP-values over larger time periods it might be considered a disadvantage that a rather reactive specie is taken as a reference.
A full evaluation of this item would require a rather careful, and detailed analysis.

From the results it can be seen that the different approaches give slightly different results in absolute values, but only marginal difference in ranking.

This similarity gives confidence that an objective ranking based on POCP-values, but taking the inherent POCP-ranges into account as well, is feasible and practical.

It should be stressed that the differences in POCP-values between the different approaches are of no importance. However, the ranges found within one model calculation, like the EMEP- and LOTOS-results, are of great importance because they reflect realistic ranges which will also be present in reality.

## 2.3 Validity of models

What is the reliability of the model calculations? In other words in how far does the calculated fixed behaviour of the $NO_x$ -VOC emissions - ozone formation and the first order estimate of x% $NO_x$- and VOC-emission reduction leading to 0.5 x % reduction of maximum ozone levels, and the exact behaviour of ozone concentrations with respect to $NO_x$ - and separate VOC-emission reduction, reflect reality.
It is fair to say that this question is still heavily debated, especially in the US (Science, 1992). However, there are strong indications that both in Los Angeles

and in Japan (Tokyo), where maximum ozone levels have hardly changed over the last decade, in spite of $NO_x$- and VOC-emission reductions of about 30 - 40%, actual behaviour of ozone, is at least not in contradiction to model results (Kuntasal and Chang, 1987, Builtjes and Stern, 1989).

A quick glance to ambient concentrations of $O_3$, NO and $NO_2$ and VOC's in the Netherlands revealed the following:

Measurements of ozone at rural stations in the Netherlands starting from 1973 do not show a trend in either the averaged level (50-percentile), or the maximum ozone levels (98-percentile). This holds also for Dutch city-stations.

VOC-measurements ($C_2$ - $C_5$) in the city of Delft show a decrease over the period 1971 - 1977, 1982 mainly in the higher percentiles. The concentration levels in 1982 are about half of the levels in the beginning of the 70's. VOC-measurements at a more rural station from 1980 onwards do not show any trend at all.

$NO_x$- concentration measurements at rural stations show no trend in NO and $NO_2$ over the period 1973 - 1978. From 1978 onwards there is a slight decrease in $NO_2$ concentrations, about 20% for the 50-percentile, and about 8% for the 98-percentile.

According to official figures, the Dutch VOC emissions increased from 1970 - 1975 from 400 kton/y to 480 kton/y, and decreased to about 420 kton/y in 1980. Over the period 1980 - 1990 there is a further decrease of about 15%.
The VOC measurements in the city of Delft are clearly locally influenced, partly also by the Rijnmond area around the harbour of Rotterdam.
So the decrease in VOC-concentrations in Delft might reflect the decrease in 'local' VOC-emissions.

The slight decrease in VOC emissions in the Netherlands over the period 1980 onwards, are not reflected in the measurement in the rural station. Obviously, this station is also influenced by VOC emissions from other countries.

The Dutch $NO_x$ emissions have increased over 1970 - 1980 from 500 kton/y to 580 kton/y, over the period 1980 onwards there is a decrease of about 10%. This decrease might be partly reflected in the decrease of $NO_2$ concentrations at rural stations over the period, but also here there will be an influence of European emissions.

With respect to European emissions, the following can be stated. Historical estimates of European (West and East) VOC- and $NO_x$ emissions have been made by Veldt (1985).
These estimates should be considered with great care. One of the largest uncertainties are the emissions, and emission trends in the eastern part of Europe. The total European VOC emissions increased from about 16 Tg/y in 1970, to 17.5 Tg/y in 1975 and to 25.5 TG/y in 1985 (see Veldt, 1992). The $NO_x$ emissions in 1970 was estimated to be 13 Tg/y, 14.5 Tg/y in 1975, in 1980 14 Tg/y and in 1985 23.2 Tg/y (Veldt, 1992).

Although these figures can only be an indication, it seems obvious that both $NO_x$- and VOC-emissions have increased over Europe over the period 1975 - 1985. It might however well be the case, that this increase has been more pronounced in the Eastern than in the Western part of Europe.

Measurements of ozone in the free troposphere over Europe, at levels above 2 - 2.5 km, show a trend over the last 30 years of an increase of about 1% per year (see for more information, Roemer, 1991).

At the moment, no detailed analysis is available of ground level ozone measurements over Europe from 1970 onwards.
Measurements are restricted mostly to the north-western part of Europe.

It is of importance to note that, although current models reflect our state-of-the-art knowledge concerning photochemical oxidant formation, the basis for the proof of the validity of the models and their results is rather weak. This weakness is due to the severe lack of reliable, Europe wide ambient measurements of ozone, and speciated VOC's.

Investigations in Europe showed that, although, like in the US, urban scale ozone formation is also present, ozone formation in Europe often is of regional to continental character. This is, to a large extent, due to the industrial band over north-western and central Europe, ranging from mid and south England to Czechoslovakia. For example, model calculations showed that on average, only 20% of ozone concentrations in the Netherlands are caused by Dutch $NO_x$ - and VOC-emissions (Builtjes and Reynolds, 1984).
In general, a consistent picture emerges from both urban and (European) regional model calculations. In the first place, the relation between the precursor emissions $NO_x$ and VOC and maximum ozone concentrations is essentially fixed. Model calculations indicate that x% emission reduction of both $NO_x$ and VOC-emissions on a European scale results in a decrease of maximum ozone levels of only about 0.5 x %. Secondly the model calculations also showed that VOC-emission reduction will always reduce maximum $O_3$-levels (with only a very few, and rather exotic exceptions like the natural VOC-specie terpene), $NO_x$-emission reduction can however locally lead to an increase in maximum ozone levels, especially down wind of high $NO_x$-emission areas (considering reaction 1, a decrease of NO can lead to a shift in the equilibrium and an increase of $O_3$; the $NO/NO_2$ ratio of emissions is always larger than 1). These results are also found in the US.

There is general consensus among model results that the best approach to reduce ozone-levels is reducing both $NO_x$- and VOC-emissions (see for example Builtjes, 1991 and the references in that paper).

Two other remarks have to be made. First, the 'exact' amount of ozone reduction resulting from emission reductions depends on the ratio of $VOC/NO_x$ concentrations in ambient air. At high ratios of $VOC/NO_x$ emission reduction of $NO_x$ is more effective than in case of a low ratio; and vice versa the emission reduction of VOC is less effective at high ratio's and more effective in case of a low ratio. Not only the ratio itself, but also the reactivity of VOC influences this effectivity (see Burton, 1988).

Secondly, an item of much investigation over the last 5 years has been the influence of natural VOC-emissions from forests on the maximum ozone levels. Although the amount of natural emissions from forests and its composition and the behaviour of these natural VOC's in the atmosphere are still rather uncertain, some remarks can be made. Natural VOC-emissions can only lead to elevated ozone levels in the presence of anthropogenic $NO_x$ and although especially in summertime at high temperatures the amount of natural VOC-emissions can be substantial, its influence does not change the general picture of the relationship between $NO_x$- and VOC-emissions and ozone as given above (see Builtjes, 1991, Derwent and Jenkin, 1990).

# 3 POCP-concept related weaknesses and knowledge gaps

## 3.1 Models and ozone measurements

Atmospheric chemists believe that their photochemical oxidant formation models are adequate to describe the contribution of VOC's to episodic ozone formation. However, they lack validation by measurements of ozone concentrations. When we accept this uncertainty an important question is whether the speciation (POCP or reactivity) of VOC's play a significant role in ozone formation, according to the models.

Based on the very limited number of only partly reliable facts the following indication can be given.
Although VOC- and $NO_x$-emissions have increased over Europe substantially over the period 1970 - 1985, maximum ozone levels revealed no obvious trend.
The emission increases are so large that, although ozone levels react only inflexible to precursor changes, an increase of ozone levels should have occurred. The reason that this is not the case might be the result of a change in composition (reactivity) of the VOC-emission. In case the reactivity of the VOC emissions has decreased substantially over 1970 - 1985, the lack of an ozone increase might be explained. However, information concerning a change in VOC-emission composition is completely lacking.
Consequently a proof of the above presented statement can not be given (there is some evidence that, although ozone has not increased, the photochemical activity of the atmosphere has increased. Dutch measurements of PAN1), which is a much more direct indication of photochemical activity, and shows a much less stiffer behaviour than ozone, show a doubling of PAN concentrations from 1975 to 1985).

In case the above given statement concerning the decrease of the VOC-reactivity which counterbalances the increase in the total VOC-emissions resulting in no obvious change in maximum ozone levels is correct, this would be a direct proof of the benefit of reducing the more reactive VOC-emission with higher priority.

Sensitivity calculations have been preformed by for example Builtjes, 1988, 1991, which clearly indicated the influence of VOC-reactivity. These calculations showed that, in case non-methane, overall antropogenic European VOC-emissions are reduced by 50%, existing maximum ozone levels reduce by 10 - 15% ($NO_x$-emissions are kept unchanged). By contrast, if emissions of the most reactive VOC-emissions are reduced with priority, in total also by 50%, (so in both runs the same amount in kg VOC-emissions is reduced, in the first run independent of the reactivity, in the second run by first taking the most reactive VOC's), the calculated result is a 20 - 30% reduction of episodic ozone levels. This means a doubling of the effectivity of the abatement strategy.

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1) PAN = peroxyacetylnitrate

It should be noted that until now, no detailed analysis of these type of results has been performed. Consequently, these findings, which are of high importance to prove the influence in general of VOC-reactivity, should be analysed in detail and followed by more specific VOC-reactivity directed model calculations.

## 3.2 Data input

Model calculations show that reactivity of VOC-emissions has a direct influence on maximum ozone levels. This can be shown as was already stated in the previous chapter by the different reaction rates of different VOC's to the OH-radical.
So, VOC-reactivity scales based on the reaction of VOC's with the OH-radical existed already at the start of the photochemical modelling activities, around 1975. However, this OH-scale has no direct link to abatement strategies. In the evaluation of the effectivity of abatement strategies the main question is which VOC-emission, on a mass basic, contributes how much to the maximum ozone levels.
To be able to determine this in an accurate way knowledge with respect to the composition of the VOC-emissions per source category is essential. Considering countrywide yearly averaged emissions, $SO_2$-emissions are the most accurate ones, followed by $NO_x$-emissions, and finally VOC-emissions. The accuracy attributed to yearly averaged VOC-emissions per country is often ± 30%, and this might even be more a wish than reality (see for example Builtjes, 1988). In addition to the uncertainty in the total mass (kg) of the VOC-emission comes the uncertainty in composition of the VOC-emissions.
Quite often, in photochemical model calculations it is assumed that VOC-emissions have a fixed composition, independent of specific source categories. This assumption is made based on the already large overall uncertainty in VOC-emissions, and the assumption that the information of VOC-composition is scarce or unreliable. Consequently, in the EMEP-emission data base, the anthropogenic VOC-emissions are split as 5.2% ethane, 16.4% ethanol, 41.5% n-butane, 2.7% ethylene, 4.8% propylene and 24.5% o-xylene, on a mass by mass basis (Simpson, 1991). Derwent and Jenkin (1991) distinguish 11 source categories with different VOC-composition based on UK-formation, and apply the same composition to the rest of Western Europe.

In the so-called PHOXA-program (photochemical oxident and acid deposition model application) an attempt has been made to use all existing information and to present the VOC-composition per source category with - if the information is available - different composition per country (Veldt, 1989).

In view of the inherent large uncertainties, until recently some reluctance was shown to perform model calculations directed to the quantitative influence of VOC-reactivity on ozone formation.

## 3.3 Long-term averaged ozone levels

The VOC-emission reduction strategies discussed at the ECE in Geneva and the EC in Brussels are restricted to their contribution to decrease ozone during episodes, so, hourly maximum ozone levels which exceed limit values. Currently, the contribution of VOC-emissions to long-term ozone levels is not mentioned in the protocols.

Long-term ozone levels have two, related, aspects. The first aspect is that the long-term, free tropospheric background ozone levels have increased over the last 50 - 100 years, and during summertime these ozone levels are at the moment 40- around 50 ppb. Consequently, episodic ozone levels are build upon an increased background. Secondly, these long-term averaged ozone levels itself exceed limit values set for the protection of vegetation. All VOC-species, and also the less reactive ones, down to CO and even $CH_4$, contribute to these background ozone levels. It can be expected that the 'POCP' for long-term averaged ozone levels is larger for less reactive VOC's than for the more reactive ones.

Until now, this aspect is not considered in legislation, although scientifically increased attention is given to this phenomenon (see for example Builtjes, 1992). A POCP-concept for long-term averaged ozone levels can most likely not straight forwardly be deducted from the episodic POCP-concept using ethylene as reference.

# 4 POCP-values of specific VOC's

In the frame of the consultancy study described in this report the question was put forward to give an estimate of the POCP-values for specific VOC's of which a list was provided by CEFIC. The basis for the estimates, presented below are the model calculations performed by Derwent (April 1991), Anderson Sköld (April 1991), Simpson (January 1991) and Builtjes (April 1991) and the reactivity with respect to the OH-radical and analogies between chemical related species.

Before the detailed list will be presented, some general remarks will be made.

It is obvious that with respect to a 'simple' POCP-based regulation a fixed table with single and simple numbers would be preferable. It has already been made clear that the inherent - and as far as current knowledge gives realistic - ranges of POCP-values per specific species inhibite such a fixed table.

However, in this chapter it is tried to present as far as possible POCP-values which are thought to reflect European(Derwent-like) POCP-calues for episodic ozone formation over a couple of days.

Before presenting a detailed table, a few remarks will be made.

In general, four groups of solvents can be distinguished, the aliphatic solvents, the aromatic solvents (sometimes these two are taken together as hydro-carbon solvents), the chlorinated solvents and the oxygenated solvents. Based on the available information with respect to POCP-values and knowing the most important solvent-species within these four groups, the following first estimate can be given:

*Table 2 POCP-estimate for different solvent groups*

| Solvents | POCP-estimate |
|---|---|
| | range |
| Aliphatic | 25 - 50 |
| Aromatic | 40 - 120 |
| Chlorinated | 1 - 7 |
| Oxygenated | 3 - 80 |

Another general remark that can be made concerns the range of POCP-values that belong to a specific species. This range is only to a minor extent due to the use of different models and (slightly) different POCP-concepts but mainly due to the inherent variability of the POCP-values as a function of meteorological conditions, $NO_x$/VOC-ratio and, VOC-reactivity within specific model calculations. In Table 3 an example of these ranges is given for ethanol.

*Table 3 POCP-ranges for ethanol*

| | **POCP of ethanol** |
|---|---|
| Derwent, original (first day) | 26.8 |
| Derwent, range | 4 - 89 |
| Anderson-Sköld 1 | 22.5 |
| Anderson-Sköld 2 | 44.6 |
| Simpson | 9 - 58 |
| Builtjes | 20 - 71 |

The original value by Derwent is based on the average POCP of the three scenarios and 9 days, the Derwent range is based on these scenarios and 11 days, Anderson-Sköld 1 results from a single source in Sweden using average difference in ozone over four days, Anderson-Sköld 2 results from a single source in Sweden producing maximum ozone difference. The Simpson result is the range of 5th-95th percentile calculated over the EMEP grid, the Builtjes result is the range of 20th-80th percentile over the LOTOS-grid (both EMEP and LOTOS cover the whole of Europe).

This example for ethanol shows the substantial range of POCP-values that belongs to a specific species. Tentatively, an average POCP-value for ethanol of 40 seems reasonable, with a range of 20-70.

In the following table, the complete list of POCP-estimates is given for the specific VOC's. By interpretating this list the above given remark made with respect to the inherent ranges should be kept in mind.

As has been mentioned, this table is meant to present POCP-values for the requested solvent-species in a manner which reflects European, multi-day photochemical oxidant formation, in a Derwent-like fashion (After consulting OSPA, a draft table was given to Derwent for comment, his answer is presented in Appendix B).

*Table 4 Classification of POCP values*

| Species | POCP | Remark |
|---|---|---|
| *POCP: 1 - 5* | | |
| perchloroethylene | 1[1,2] | |
| 1,1,1-trichlorethane | 1 | based on OH-reactivity |
| dichloromethane | 1 | based on OH-reactivity |
| methylacetate | 3 | based on OH-reactivity |
| acetonitrile | 5 | based on OH-reactivity |
| *POCP: 6 - 20* | | |
| trichloroethylene | 7[1,2] | |
| methanol | 10[1] | |
| isopropanol | 15[1] | |
| butanoic acid, 3-oxo-methyl ester | 20 | analogy with acetone |
| 2-pentanone, 4-hydroxy-4-methyl | 20 | analogy with acetone |
| acetone | 20[1] | |
| ethyl-acetate | 20[1] | |
| methane,-oxybis- | 20 | dimethylether |
| *POCP: 21 - 35* | | |
| ethanol | 25[1] | |
| cyclohexane | 25[1] | |
| 1,2-propanediol | 30 | analogy with but-2-diol |
| 2,4 pentanediol, 2-methyl | 30 | analogy with propylene-glycol |
| acetic acid, 1-methylethyl ester | 30 | analogy with ethyl acetate and i-butylacetate |
| 2-propanol, 1-methoxy-acetate (PMA) | 30 | propylene glycol methyl ether acetate |
| 1-butanol, 3-methoxy-acetate | 30 | analogy with propylene glycol methyl ether acetate |
| 2,2,4 tri-methylpentane | 30 | analogy with iso-pentane |
| i-butyl acetate | 35[1] | |
| methylcyclohexane | 35[1] | |
| acetic acid, 2-methylpropyl ester (i-butylacetate) | 35[1] | |
| *POCP: 36 - 50* | | |
| 3-pentanone | 40 | analogy with methyl-ethyl ketone and propane, butane series |
| i-butanol | 40 | |
| ethanol, 2-methoxy-acetate | 40 | POCP a bit higher than propylene glycol methyl ether acetate |
| methyl-ethyl ketone (MEK) | 40[1] | |
| 2-methyl, 3-phenyl butane | 40 | |
| butyl cyclohexane | 40 (?) | C10 cyclo alkanes |
| 1,2,4-tri-methyl cyclohexane | 40 | analogy with methyl-, ethyl-cyclohexane |
| tetra methyl cyclohexane | 40 | C10 cyclo alkanes |

*Table 4 Classification of POCP values (Continued)*

| Species | POCP | Remark |
|---|---|---|
| ethyl-dimethyl cyclohexane | 40 | C10 cyclo alkanes |
| 1,3 diethyl cyclohexane | 40 | C10 cyclo alkanes |
| n-hexane | 40 1) | |
| butylbenzene | 45 | C10 mono substituted benzene |
| n-buthyl-acetate | 45 1) | |
| 1,1 dimethyl cyclopentane | 45 | C10 mono substituted benzene |
| 3-methyl pentane | 45 1) | |
| isodecanol | 45 | analogy with n-decane |
| n-propanol | 45 1) | |
| propane, 2,2-oxybis- | 50 | analogy with ethyl t-butylether |
| 2-ethylhexyl ester | 50 | analogy with 2-methylhexane |
| 2-methyl hexane | 50 1) | |
| 2-methyl pentane | 50 1) | |
| *POCP: 51 - 65* | | |
| toluene | 55 1) | |
| 1-butanol | 55 | |
| 2-butanol | 55 1) | analogy with n-butanol |
| 1-hexanol, 2-ethyl- | 55 | analogy with n-butanol and n-heptane |
| 2-pentanol, 4-methyl- | 55 | analogy with n-butanol |
| n-butanol | 55 1) | |
| ethanol, 2-butoxy-acetate | 60 | analogy with ethylglycolether acetate |
| ethanol, 2-ethoxy-acetate | 60 | (ethylglycolether acetate) |
| ethane, 1,1-oxybis- | 60 | analogy with ethyl t-buthyl ether (more reactive) |
| ethoxy propyl-acetate | 65 | analogy with ethyl-glycol acetate |
| o-xylene | 65 1) | |
| 1-methyl, 4-propyl-benzene | 65 | C10 disubstituted benzene |
| *POCP: 66 - 80* | | |
| ethanol, 2-methoxy- (methyl glycolether) | 70 | methyl glycol ether |
| furan, tetrahydro | 70 | compare with cyclopentane and series methyl - buthyl ether → ethyl - buthyl ether |
| ethanol, 2-ethoxy (ethyl glycolether) | 75 | analogy with propylene glycol ether |
| ethanol, 2-butoxy (butyl glycolether) | 80 | analogy with propylene glycol ether |
| 1-methyl, 3-ethyl benzene | 80 | m-ethyltoluene |
| 2-cyclohexene-1-one, 3,5,5-trimethyl | 80 (?) | based on OH-reactivity |
| 2-propanol, 1-methoxy (PM) | 80 | propylene, glycol methylether |
| 4-heptanone, 2,6-dimethyl- | 80 | analogy with methyl i-butylketon and higher reactivity |
| propanol, methoxy- | 80 | propylene glycol methyl ether |

*Table 4 Classification of POCP values (Continued)*

| Species | POCP | Remark |
|---|---|---|
| *POCP: 81 - 95* | | |
| ethoxy propanol | 85 | analogy with propylene glycol methylether |
| diglycolethers | 90 (?) | |
| triglycolethers | 90 (?) | |
| p-xylene | 90 $^{1)}$ | |
| 1,3-diethyl benzene | 95 | analogy with m-xylene |
| *POCP: 96 - 120* | | |
| ethyl trimethyl benzene | 110 (?) | a bit less than C11 trisubstituted benzene |
| tetra methyl benzene | 110 | a bit less than trimethyl benzene |
| ethyl dimethyl benzene | 115 | C10 trisubstituted benzene |
| 1,2,4-trimethyl benzene | 120 $^{1)}$ | |
| diethyl methyl benzene | 120 | C11 trisubstituted benzene |

| | | |
|---|---|---|
| 1) | Derwent, R.G. | 'Photochemical Ozone Creation Potentials, for over 150 individual organic compounds'. Air Quality division, Department of the Environment, UK, April 1991'. |
| 2) | Derwent, R.G. and M.E. Jenkin | 'Hydrocarbons and the long-range transport of ozone and PAN across Europe'. Atm. Env. $25^A$, 8, 1661-1678, 1991. |

Five different kind of remarks are used in the table:
- blank no remark; the POCP is taken from the references,
- just a name; the compound is equivalent to the one mentioned under remark and for which a POCP from the references is available,
- analogy with: the chemically most related compound is taken as base for the estimate,
- based on OH-activity. Only the reactivity of the compound is considered,
- unknown.

The uncertainty of POCP's in the first two categories is given in the references. Estimates in the other three categories are increasingly more uncertain.
Table 4 shows the classification of species by defining POCP categories with a range of 15. The first category, with the lowest, values is defined for all species with POCP's smaller than or equal to 5. The highest category is for all species with POCP beyond 95.

In this Table 4 only averaged, mean POCP-values are given. For a number of VOC-species no POCP-estimate could be given at all, due to lack of basic chemical kinetics information. At the moment, some experiments are performed at the Univ. of Leeds (see Appendix B) to estimate OH-rate coefficients for specific VOC's.

Obviously, the question arises by which difference between POCP-values the difference can be considered as significant. In principle, before giving such an estimate, POCP-model calculations including these inherent range, like model calculations with LOTOS, should be performed. However, as an indication it seems likely that at POCP-values of 30 - 80 only two species with a POCP-value which differs more than 10 - 15 can be considered as significantly different in POCP-value.

The reliability of the table could be improved by performing LOTOS-POCP calculations for a number of the most important solvents, which are representative of a class of solvents.

# 5 Emission reduction: flat rate or POCP-based

Concerning the item in how far a POCP-based VOC-emission reduction is preferable to a flat rate VOC-emission reduction already quite a number of remarks have been made in the previous chapters. Here, in summary, the following can be stated.

- There is general concensus that anthropogenic VOC-emission reductions are useful, and required, to reduce episodic ozone levels. In the literature, often VOC-emission reductions fo 70 - 90% are mentioned, relative to 1985 emissions, to be able to bring ozone levels below existing guidelines.

- There is general concensus that the differences in reactivity of VOC-species lead to differences in ozone formation. Consequently, the POCP-concept is in principle valid as a method of ranking VOC-species.

- Because ranking according to a POCP-scale is valid and possible, a POCP-based emission reduction is to be preferred above a flat rate emission reduction.

- A final and definite ranking is hampered by two different aspects, which are of different nature.
  - Calculated POCP-values of VOC-species show an inherent range, instead of one fixed value. One of the major reasons for this range is the existing differences in $NO_x$- and VOC-emissions over Europe. These ranges in POCP-values are real, and will **not** be reduced with increasing insight.
  - The experience in calculating and estimating POCP-values is limited. Calculations using this concept have only been performed in Europe by the end of 1990, and only four European groups have actively participated in POCP-calculations. It is clear that by further research progress can be made concerning the possibilities, and impossibilities of the POCP-concept.

- Nevertheless, general grouping of solvents according to the POCP-concept is feasable. However, a more refined classification is either fundamentally impossible in case the differences in 'POCP-values are too small, or can not be performed by lack of information and/or lack of model results.

# 6 POCP based legislation

## 6.1 Introduction

VOC-emission reduction strategies are being discussed in Europe at two levels, at the ECE in Geneva, and the EC in Brussels.

The UNECE VOC-protocol, and its technical annexes, is signed in November 1991 and, in general terms, aims at a VOC-emission reduction of 30% relative to 1985, by the year 2000. This 30% is on a mass basis. The POCP-concept, as described in Annex IV of the protocol (here Appendix A) is formulated as a guidance which can be used, but not as a requirement.

The EC is in the process of drafting a VOC-legislation.

How could the POCP-concept be used for VOC-legislation?

From the foregoing chapters it follows that POCP values of solvents show a range that has its origin in the formation of ozone in the atmosphere at different places, meteorological conditions etc. Different models may show variations in the exact values of the range but these variations are minor compared to the range itself.

It was also concluded that the POCP values of some solvents are not known very well. This is a result of the fact that no POCP calculations were performed for this solvent due to lack of interest or lack of important data (especially reactivity data). The given POCP values (in Table 4) are based on the best estimates that can be made at this moment. When more data come available progress can be made towards elimination of the uncertainty.

Experts on atmospheric chemistry agree that the reactivity of VOC's is an important factor in the formation of episodic ozone. It is not expected that new information on emissions or speciation of emissions will change the concept of the influence of reactivity on ozone formation. Therefore, the important question is whether we can use the POCP concept for the formulation of legislation aiming at a reduction of troposheric ozone formation during episodes. In this chapter the posibillities for POCP based legislation will be investigated. We will concentrate on the emission reduction of VOC's from industrial applications. Consumption of products from which solvents evaporate into the air can't be controlled otherwise than by reformulation to less, or different, solvent containing products.

## 6.2 Legislation options in general

There are several options for formulating legislation for VOC emission reduction. The most structured and clear approach is defining Emission Limit Values (ELV's), the concept of many national legislations such as the TA-Luft Guidelines in the Federal Republic of Germany. One can classify VOC's and define ELV's that become stricter for different classes. The classifications used nowadays are based on toxicological and (expected) carcinogenic effects of the VOC's on people.

The second option is not a real form of legislation but more a project, an agreement between an administration and the industry on the reduction of VOC emissions. This option is favoured in The Netherlands and worked out in the project 'Hydrocarbons 2000'. An important aspect in this project is the strong preference for substitution of VOC's, mostly being solvents, by non-VOC containing products. This approach gives a large flexibility and motivation but is hard to monitor and control.

Other possibilities for emission reduction legislation are the use of Emission Factors (i.e. g emission/kg product) and the flexible use of a bubble concept (also called balloon approach), such as in use in the United States of America. The concept of a Solvent Management Plan, now under study by the European Commission, can be regarded as a strong tool for most forms of legislation, giving information and possibly regulating measures. The problem of investigating fugitive emissions can be solved by a Solvent Management Plan.

## 6.3 POCP based legislation

POCP values of solvents can be used to classify the solvents into classes associated with Emission Limit Values. Based on the overall range of POCP values from 1 to 120, and considering 15 as a minimum difference to be significant, 7 to 8 classes would be possible. In national ELV based legislations in the European Community only three classes are used, with one exeption (Italy uses five classes), so a further diversification into more than three classes will need adaptation by national administrations. Another option when using ELV's, is weighting the emitted mass by the POCP values of the solvents, so that high POCP valued solvents have a weight factor higher than 1. In fact this means that one would introduce a 'hidden' classification within another classification. This would make the regulation more complex. It is also possible to use more than one list with classifications. Furthermore the choice of a reference point and the weighting factors need consensus. However, there are advantages in introducing reactivity (POCP) within a mass based reduction philosophy. The resulting decrease in ozone concentrations during episodes will be more pronounced. A first move to implement reactivity in legislation was presented by the protocol on VOC's in Geneva, see Appendix A.

Another option would be the incorporation of POCP values into a substitution approach. This would mean that preference is given to a solvent that has a lower POCP value, preferably by at least two classes of the 7 or 8 mentioned earlier, in the formulation of a product. With this option the POCP values can be used to their full extent in the reformulation of new solvents replacing old ones with higher POCP values. However, this does not mean that a mass based reduction of VOC emissions is no longer necessary. Reformulation of solvents based on POCP values has to be regarded as a tool to make a mass reduction more effective.

The same reasoning can be applied to other forms of legislation mentioned in the foregoing section. The balloon approach as a concept does not really differ from the viewpoint of introducing a POCP weighted mass. Consensus on weight factors and reference point is needed. A single reformulation of solvents to low POCP values, as far as possible, will probably have a too small effect on episodic ozone formation to reach the acceptable treshold levels. It is possible to calculate the effect of a shift in the reactivity on ozone formation for proposed scenarios. A realistic scenario needs an input on technical feasibility of proposed shifts, by experts on solvents.

At this moment there is no example of an evaluation of legislation for VOC emission reduction based on a reactivity approach.

# 7 Conclusions and recommendations

From the results presented in this report the following conclusions can be drawn.

- Because different VOC-species have a different reaction rate with the OH-radical, different VOC-species will influence episodic ozone information in a different way, which makes a VOC-classification in principle possible.
- Model calculations indicate a rather fixed behaviour of episodic ozone trends following a change in the precursur emissions VOC and $NO_x$ on a mass basis. The trends in VOC- and $NO_x$-emissions, and ozone concentrations in both Los Angeles and Tokyo are at least not in contradiction with these model results.
- Model calculations indicate a rather substantial influence of VOC-speciation on episodic ozone levels. The trends in VOC- and $NO_x$-emissions and ozone concentrations show that this influence might present reality.
- The concept of photochemical ozone creation potential (POCP) is scientifically sound, and POCP-values for different VOC's can be calculated by appropriate models.
- POCP-calculations show that POCP-values have an inherent range which also exists in reality. These ranges hamper a detailed ranking of VOC's based on their POCP-value. However, a more general ranking is definitly possible.

The results presented in this report, indicate weaknesses and gaps in knowledge with respect to the POCP-approach. This leads to the following recommendations.

- Studies of the POCP-concept only started by the end of 1990. Consequently, there is limited experience with this concept, and there is an urgent need for a number of more basic studies into this phenomenon.
- The uncertainty in the VOC-emissions on a mass-basis, and the large uncertainty in their speciation, hampers a more accurate and reliable calculation of POCP-values. To be able to calculate POCP for solvents in a more reliable way the VOC-speciation should be known better than until now. Detailed information concerning VOC-speciation should become available.
- The model calculations show a substantial range in POCP-values per VOC. This range is influenced by the spatial gradients in $NO_x$- and VOC-emissions, and their ratio, meteorological conditions and by the influence of natural emissions. It is unknown how large the influence of the different aspects is. Model calculations should be performed to reveal this influence, which enables the set-up of a more condensed POCP-range by eliminating certain influences.
- The POCP-concept is restricted to episodic ozone formation. VOC-emissions however also influence long term average ozone formation. Also for this aspect POCP-values should be considered, and an optimal abatement strategy should combine episodic and long term averaged POCP-rankings.
- The set-up of a European solvent emission abatement strategy might benefit from a close consideration of the experience in California and Japan.
- The 'definite' ranking of VOC's using the POCP-approach will require a close cooperation between the regulatory community and the scientific community, in view of the impossibility of presenting one fixed POCP-value per VOC-species.

- The POCP-values, presented in this report for the specific VOC's are estimates following the Derwent approach. A more sound and reliable basis for POCP-values, including their inherent range, can be provided by performing LOTOS-model calculations or calculations by a similar model. It seems appropiate to perform such calculation for a selected number of essential solvent species.
- Legislation aiming at a reduction of ozone formation will benefit from a more pronounced abatement of high POCP compounds, added to a mass reduction of VOC emissions. This approach has not yet been worked out in any legislation adressed to VOC emission reduction.

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# 9 Authentication

Name and address of the principal
Oxygenated Solvents Producers Association
Av. E. van Nieuwenhuyse 4, bte 2
B 1160 Brussels
Belgium
Attention Mr. P. Teheux

Names and functions of the cooperators
P.J.H. Builtjes / M.G.M. Roemer / A.C. Baart

Names of establishments to which part of the research was put out to contract
–

Date upon which, or period in which, the research took place
December 1991 - April 1992

| Signature | Approved by |
|---|---|
| Ir. D.C. Heslinga<br>research coordinator | Ir. J.I. Walpot<br>section leader |

# Appendix A Annex IV: UNECE protocol Geneva

# ANNEX IV

## CLASSIFICATION OF VOLATILE ORGANIC COMPOUNDS (VOCs) BASED ON THEIR PHOTOCHEMICAL OZONE CREATION POTENTIAL (POCP)

1. This annex summarizes the information available and identifies the still existing elements to develop in order to guide the work to be carried out. It is based on information regarding hydrocarbons and ozone formation contained in two notes prepared for the Working Group on Volatile Organic Compounds (EB.AIR/WG.4/R.11 and R.13); on the results of further research carried out, in particular in Austria, Canada, Germany, Netherlands, Sweden, the United Kingdom, the United States of America and the EMEP Meteorological Synthesizing Centre-West (MSC-W); and on supplementary information provided by governmentally designated experts.

2. The final aim of the POCP approach is to provide guidance on regional and national control policies for volatile organic compounds (VOCs), taking into account the impact of each VOC species as well as sectoral VOC emissions in episodic ozone formation expressed in terms of the photochemical ozone creation potential (POCP), which is defined as the change in photochemical ozone production due to a change in emission of that particular VOC. POCP may be determined by photochemical model calculations or by laboratory experiments. It serves to illustrate different aspects of episodic oxidant formation; e.g. peak ozone or accumulated ozone production during an episode.

3. The POCP concept is being introduced because there is a large variation between the importance of particular VOCs in the production of ozone during episodes. A fundamental feature of the concept is that, in the presence of sunlight and $NO_x$, each VOC produces ozone in a similar way despite large variations in the circumstances under which ozone is produced.

4. Different photochemical model calculations indicate that substantial reduction of VOCs and $NO_x$ emissions are necessary (order of magnitude above 50% in order to achieve significant ozone reduction). Moreover the maximum concentrations of ozone near the ground are reduced in a less than proportional way when VOC emissions are reduced. This effect is shown in principle by theoretical scenario calculation. When all species are reduced by the same proportion, maximum ozone values (above 75 ppb hourly average) in Europe are reduced depending on the existing ozone level by only 10-15% if the mass of non-methane man-made VOC emissions is reduced by 50%. By contrast, if emissions of the most important (in terms of POCP and mass values or reactivity) non-methane man-made VOC species were reduced by 50% (by mass), the calculated result is a 20-30% reduction of peak episodic ozone concentration. This confirms the merits of a POCP approach to determine priorities for VOC emission control and clearly shows that VOCs may at least be divided into large categories, according to their importance in episodic ozone formation.

5. POCP values and reactivity scales have been calculated as estimates, each based on a particular scenario (e.g. emission increases and decreases, air mass trajectories) and targeted towards a particular objective (e.g. peak ozone concentration, integrated ozone, average ozone). POCP values and reactivity scales are dependent on chemical mechanisms. Clearly there are

differences between the different estimates of POCPs, which in some cases can span more than a factor of four. The POCP numbers are not constant but vary in space and time. To give an example: the calculated POCP of ortho-xylene in the so-called "France-Sweden" trajectory has a value of 41 on the first day and of 97 on the fifth day of the travelling time. According to calculations of the Meteorological Synthesizing Centre-West (MSC-W) of EMEP, the POCP of ortho-xylene for $O_3$ over 60 ppb, varies between 54 and 112 (5 to 95 percentiles) for the grids of the EMEP area. The variation of the POCP in time and space is not only caused by the VOC composition of the air parcel due to man-made emissions but is also a result of meteorological variations. The fact is that any reactive VOC can contribute to the episodical formation of photochemical oxidants to a higher or lower extent, depending on the concentrations of $NO_x$ and VOC and meteorological parameters. Hydrocarbons with very low reactivity, like methane, methanol, ethane and some chlorinated hydrocarbons contribute in a negligible manner to this process. There are also differences as a result of meteorological variations between particular days and over Europe as a whole. POCP values are implicitly dependent on how emission inventories are calculated. Currently there is no consistent method or information available across Europe. Clearly, further work has to be done on the POCP approach.

6. Natural isoprene emissions from deciduous trees, together with nitrogen oxides ($NO_x$) mainly from man-made sources, can make a significant contribution to ozone formation in warm summer weather in areas with a large coverage of deciduous trees.

7. In table 1, VOC species are grouped according to their importance in the production of episodic peak ozone concentrations. Three groups have been selected. Importance in Table 1 is expressed on the basis of VOC emission per unit mass. Some hydrocarbons, such as n-butane, become important because of their mass emission although they may not appear so according to their OH reactivity.

8. Tables 2 and 3 show the impacts of individual VOCs expressed as indices relative to the impact of a single species (ethylene) which is given an index of 100. They indicate how such indices, i.e. POCPs, may give guidance for assessing the impact of different VOC emission reductions.

9. Table 2 shows averaged POCPs for each major source category based on a central POCP estimate for each VOC species in each source category. Emission inventories independently determined in the United Kingdom and Canada have been used in this compilation and presentation. For many sources, e.g. motor vehicles, combustion installations, and many industrial processes mixtures of hydrocarbons are emitted. Measures to reduce specifically the VOC compounds identified in the POCP approach as very reactive are in most cases unavailable. In practice, most of the possible reduction measures will reduce emissions by mass irrespective of their POCPs.

10. Table 3 compares a number of different weighting schemes for a selected range of VOC species. In assigning priorities within a national VOC control programme, a number of indices may be used to focus on particular VOCs. The simplest but least effective approach is to focus on the relative mass emission, or relative ambient concentration.

### TABLE 1. CLASSIFICATION OF VOCs INTO THREE GROUPS ACCORDING TO THEIR IMPORTANCE IN EPISODIC OZONE FORMATION

| | |
|---|---|
| More important | |
| Alkenes | |
| Aromatics | |
| Alkanes | > C6 alkanes except 2,3 dimethylpentane |
| Aldehydes | All aldehydes except benzaldehyde |
| Biogenics | Isoprene |
| Less important | |
| Alkanes | C3 - C5 alkanes and 2,3 dimethylpentane |
| Ketones | Methyl ethyl ketone and methyl t-butyl ketone |
| Alcohols | Ethanol |
| Esters | All esters except methyl acetate |
| Least important | |
| Alkanes | Methane and ethane |
| Alkynes | Acetylene |
| Aromatics | Benzene |
| Aldehydes | Benzaldehyde |
| Ketones | Acetone |
| Alcohols | Methanol |
| Esters | Methyl acetate |
| Chlorinated hydrocarbons | Methyl chloroform,<br>Methylene chloride,<br>Trichloroethylene and tetrachloroethylene |

11. Relative weighting based on OH reactivity addresses some but by no means all of the important aspects of the atmospheric reactions which generate ozone in the presence of $NO_x$ and sunlight. The SAPRC (Statewide Air Pollution Research Centre) weightings address the situation in California. Because of differences in the model conditions appropriate to the Los Angeles basin and Europe, major differences in the fates of photochemical, labile species, such as aldehyde, result. POCPs calculated with photochemical models in the Netherlands, United States of America, United Kingdom, Sweden and by EMEP (MSC-W) address different aspects of the ozone problem in Europe.

12. Some of the less-reactive solvents cause other problems, e.g. they are extremely harmful to human health, difficult to handle, persistent, can cause negative environmental effects at other levels (e.g. in the free troposphere or the stratosphere). In many cases the best available technology for reducing solvent emission is the application of non-solvent using systems.

13. Reliable VOC emission inventories are essential to the formulation of any cost-effective VOC control policies and in particular those based on the POCP approach. National VOC emissions should therefore be specified according to sectors, at least following guidelines specified by the Executive Body, and should as far as possible be complemented by data on species and time variations of emissions.

TABLE 2. SECTORAL POCPs OF THE VARIOUS EMISSION SECTORS AND THE PERCENTAGE BY MASS OF VOCs IN EACH OZONE CREATION CLASS

| Sector | Sectoral POCP | | Percentage mass in each ozone creation class | | | |
|---|---|---|---|---|---|---|
| | Canada | United Kingdom | More Important | Less Important | Least Important | Unknown |
| Petrol-engined vehicle exhaust | 63 | 61 | 76 | 16 | 7 | 1 |
| Diesel vehicle exhaust | 60 | 59 | 38 | 19 | 3 | 39 |
| Petrol-engined vehicle evaporation | - | 51 | 57 | 29 | 2 | 12 |
| Other transport | 63 | - | - | - | - | - |
| Stationary combustion | - | 54 | 34 | 24 | 24 | 18 |
| Solvent usage | 42 | 40 | 49 | 26 | 21 | 3 |
| Surface coating | 48 | 51 | - | - | - | - |
| Industrial process emissions | 45 | 32 | 4 | 41 | 0 | 55 |
| Industrial chemicals | 70 | 63 | - | - | - | - |
| Petroleum refining and distribution | 54 | 45 | 55 | 42 | 1 | 2 |
| Natural gas leakage | - | 19 | 24 | 8 | 66 | 2 |
| Agriculture | - | 40 | - | - | 100 | - |
| Coal mining | - | 0 | - | - | 100 | - |
| Domestic waste landfill | - | 0 | - | - | 100 | - |
| Dry cleaning | 29 | - | - | - | - | - |
| Wood combustion | 55 | - | - | - | - | - |
| Slash burn | 58 | - | - | - | - | - |
| Food industry | - | 37 | - | - | - | - |

TABLE 3. COMPARISON BETWEEN WEIGHTING SCHEMES (EXPRESSED RELATIVE TO ETHYLENE = 100) FOR 85 VOC SPECIES

| VOC | OH Scale [a] | Canada by mass [b] | SAPRAC MIR [c] | UK POCP [d] | UK range [e] | Sweden | | EMEP [h] | LOTOS [i] |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | max. diff. [f] | 0-4 days [g] | | |
| Methane | 0.1 | - | 0 | 0.7 | 0-3 | - | - | - | - |
| Ethane | 3.2 | 91.2 | 2.7 | 8.2 | 2-30 | 17.3 | 12.6 | 5-24 | 6-25 |
| Propane | 9.3 | 100 | 6.2 | 42.1 | 16-124 | 60.4 | 50.3 | - | - |
| n-Butane | 15.3 | 212 | 11.7 | 41.4 | 15-115 | 55.4 | 46.7 | 22-85 | 25-87 |
| i-Butane | 14.2 | 103 | 15.7 | 31.5 | 19-59 | 33.1 | 41.1 | - | - |
| n-Pentane | 19.4 | 109 | 12.1 | 40.8 | 9-105 | 61.2 | 29.8 | - | - |
| i-Pentane | 18.8 | 210 | 16.2 | 29.6 | 12-68 | 36.0 | 31.4 | - | - |
| n-Hexane | 22.5 | 71 | 11.5 | 42.1 | 10-151 | 78.4 | 45.2 | - | - |
| 2-Methylpentane | 22.2 | 100 | 17.0 | 52.4 | 19-140 | 71.2 | 52.9 | - | - |
| 3-Methylpentane | 22.6 | 47 | 17.7 | 43.1 | 11-125 | 64.7 | 40.9 | - | - |
| 2,2-Dimethylbutane | 10.5 | - | 7.5 | 25.1 | 12-49 | - | - | - | - |
| 2,3-Dimethylbutane | 25.0 | - | 13.8 | 38.4 | 25-65 | - | - | - | - |
| n-Heptane | 25.3 | 41 | 9.4 | 52.9 | 13-165 | 79.1 | 51.8 | - | - |
| 2-Methylhexane | 18.4 | 21 | 17.0 | 49.2 | 11-159 | - | - | - | - |
| 3-Methylhexane | 18.4 | 24 | 16.0 | 49.2 | 11-157 | - | - | - | - |
| n-Octane | 26.6 | - | 7.4 | 49.3 | 12-151 | 69.8 | 46.1 | - | - |
| 2-Methylheptane | 26.6 | - | 16.0 | 46.9 | 12-146 | 69.1 | 45.7 | - | - |
| n-Nonane | 27.4 | - | 6.2 | 46.9 | 10-148 | 63.3 | 35.1 | - | - |
| 2-Methyloctane | 27.3 | - | 13.2 | 50.5 | 12-147 | 66.9 | 45.4 | - | - |
| n-Decane | 27.6 | - | 5.3 | 46.4 | 8-156 | 71.9 | 42.2 | - | - |
| 2-Methylnonane | 27.9 | - | 11.7 | 44.8 | 8-153 | 71.9 | 42.3 | - | - |
| n-Undecane | 29.6 | 21 | 4.7 | 43.6 | 8-144 | 66.2 | 38.6 | - | - |
| n-Duodecane | 28.4 | - | 4.3 | 41.2 | 7-138 | 57.6 | 31.1 | - | - |
| Methylcyclohexane | 35.7 | 18 | 22.3 | - | - | 40.3 | 38.6 | - | - |
| Methylene chloride | - | - | - | 1 | 0-3 | 0 | 0 | - | - |
| Chloroform | - | - | - | - | - | 0.7 | 0.4 | - | - |
| Methyl chloroform | - | - | - | 0.1 | 0-1 | 0.2 | 0.2 | - | - |
| Trichloroethylene | - | - | - | 6.6 | 1-13 | 8.6 | 11.1 | - | - |
| Tetrachloroethylene | - | - | - | 0.5 | 0-2 | 1.4 | 1.4 | - | - |
| Allyl chloride | - | - | - | - | - | 56.1 | 48.3 | - | - |
| Methanol | 10.9 | - | 7 | 12.3 | 9-21 | 16.5 | 21.3 | - | - |
| Ethanol | 25.5 | - | 15 | 26.8 | 4-89 | 44.6 | 22.5 | 9-58 | 20-71 |
| i-Propanol | 30.6 | - | 7 | - | - | 17.3 | 20.3 | - | - |
| Butanol | 38.9 | - | 30 | - | - | 65.5 | 21.4 | - | - |
| i-Butanol | 45.4 | - | 14 | - | - | 38.8 | 25.5 | - | - |
| Ethylene glycol | 41.4 | - | 21 | - | - | - | - | - | - |
| Propylene glycol | 55.2 | - | 18 | - | - | - | - | - | - |
| But-2-diol | - | - | - | - | - | 28.8 | 6.6 | - | - |
| Dimethyl ether | 22.3 | - | 11 | - | - | 28.8 | 34.3 | - | - |
| Methyl-t-butyl ether | 11.1 | - | 8 | - | - | - | - | - | - |
| Ethyl-t-butyl ether | 25.2 | - | 26 | - | - | - | - | - | - |
| Acetone | 1.4 | - | 7 | 17.8 | 10-27 | 17.3 | 12.4 | - | - |
| Methyl ethyl ketone | 5.5 | - | 14 | 47.3 | 17-80 | 38.8 | 17.8 | - | - |
| Methyl-i-butyl ketone | - | - | - | - | - | 67.6 | 31.8 | - | - |
| Methyl acetate | - | - | - | 2.5 | 0-7 | 5.8 | 6.7 | - | - |
| Ethyl acetate | - | - | - | 21.8 | 11-56 | 29.5 | 29.4 | - | - |
| i-Propyl acetate | - | - | - | 21.5 | 14-36 | - | - | - | - |
| n-Butyl acetate | - | - | - | 32.3 | 14-91 | 43.9 | 32.0 | - | - |
| i-Butyl acetate | - | - | - | 33.2 | 21-59 | 28.8 | 35.3 | - | - |
| Propylene glycol methyl Ether | - | - | - | - | - | 77.0 | 49.1 | - | - |
| Propylene glycol methyl Ether acetate | - | - | - | - | - | 30.9 | 15.7 | - | - |

TABLE 3 (continued)

| VOC | OH Scale | Canada by mass | SAPRAC MIR | UK POCP | UK POCP Range | Sweden max. diff. | Sweden 0-4 days | EMEP | LOTOS |
|---|---|---|---|---|---|---|---|---|---|
| Ethylene | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Propylene | 217 | 44 | 125 | 103 | 75-163 | 73.4 | 59.9 | 69-138 | 55-120 |
| 1-Butene | 194 | 32 | 115 | 95.9 | 57-185 | 79.9 | 49.5 | - | - |
| 2-Butene | 371 | - | 136 | 99.2 | 82-157 | 78.4 | 43.6 | - | - |
| 1-Pentene | 148 | - | 79 | 105.9 | 40-288 | 72.7 | 42.4 | - | - |
| 2-Pentene | 327 | - | 79 | 93.0 | 65-160 | 77.0 | 38.1 | - | - |
| 2-Methyl-1-butene | 300 | - | 70 | 77.7 | 52-113 | 69.1 | 18.1 | - | - |
| 2-Methyl-2-butene | 431 | 24 | 93 | 77.9 | 61-102 | 93.5 | 45.3 | - | - |
| 3-Methyl-1-butene | 158 | - | 79 | 89.5 | 60-154 | - | - | - | - |
| Isobutene | 318 | 50 | 77 | 64.3 | 58-76 | 79.1 | 58.0 | - | - |
| Isoprene | 515 | - | 121 | - | - | 53.2 | 58.3 | - | - |
| Acetylene | 10.4 | 82 | 6.8 | 16.8 | 10-42 | 27.3 | 36.8 | - | - |
| Benzene | 5.7 | 71 | 5.3 | 18.9 | 11-45 | 31.7 | 40.2 | - | - |
| Toluene | 23.4 | 218 | 34 | 56.3 | 41-83 | 44.6 | 47.0 | - | - |
| o-Xylene | 48.3 | 38 | 87 | 66.6 | 41-97 | 42.4 | 16.7 | 54-112 | 26-67 |
| m-Xylene | 80.2 | 53 | 109 | 99.3 | 78-135 | 58.3 | 47.4 | - | - |
| p-Xylene | 49.7 | 53 | 89 | 88.8 | 63-180 | 61.2 | 47.2 | - | - |
| Ethylbenzene | 25 | 32 | 36 | 59.3 | 35-114 | 53.2 | 50.4 | - | - |
| 1,2,3-Trimethyl benzene | 89 | - | 119 | 117 | 76-175 | 69.8 | 29.2 | - | - |
| 1,2,4-Trimethyl benzene | 107 | 44 | 119 | 120 | 86-176 | 68.3 | 33.0 | - | - |
| 1,3,5-Trimethyl benzene | 159 | - | 140 | 115 | 74-174 | 69.1 | 33.0 | - | - |
| o-Ethyltoluene | 35 | - | 96 | 66.8 | 31-130 | 59.7 | 40.8 | - | - |
| m-Ethyltoluene | 50 | - | 96 | 79.4 | 41-140 | 62.6 | 40.1 | - | - |
| p-Ethyltoluene | 33 | - | 96 | 72.5 | 36-135 | 62.6 | 44.3 | - | - |
| n-Propylbenzene | 17 | - | 28 | 49.2 | 25-110 | 51.1 | 45.4 | - | - |
| i-Propylbenzene | 18 | - | 30 | 56.5 | 35-105 | 51.1 | 52.3 | - | - |
| Formaldehyde | 104 | - | 117 | 42.1 | 22-58 | 42.4 | 26.1 | - | - |
| Acetaldehyde | 128 | - | 72 | 52.7 | 33-122 | 53.2 | 18.6 | - | - |
| Proprionaldehyde | 117 | - | 87 | 60.3 | 28-160 | 65.5 | 17.0 | - | - |
| Butyraldehyde | 124 | - | - | 56.8 | 16-160 | 64.0 | 17.1 | - | - |
| i-Butyraldehyde | 144 | - | - | 63.1 | 38-128 | 58.3 | 30.0 | - | - |
| Valeraldehyde | 112 | - | - | 68.6 | 0-268 | 61.2 | 32.1 | - | - |
| Acrolein | - | - | - | - | - | 120.1 | 82.3 | - | - |
| Benzaldehyde | 43 | - | -10 | -33.4 | -82-(-12) | - | - | - | - |

[a] OH + VOC rate coefficient divided by molecular weight.

[b] Ambient VOC concentrations at 18 sites in Canada expressed on mass basics.

[c] Maximum Incremental Reactivity (MIR) based on California scenarios; Statewide Air Pollution Research Centre, Los Angeles, USA.

[d] Average POCP based on three scenarios and 9 days; FRG-Ireland, France-Sweden and UK.

[e] Range of POCPs based on three scenarios and 11 days.

[f] POCPs calculated for a single source in Sweden producing maximum ozone difference.

[g] POCPs calculated for a single source in Sweden using average difference in ozone over 4 days.

[h] Range (5th-95th percentile) of POCPs calculated over EMEP grid.

[i] Range (20th-80th percentile) of POCPs calculated over LOTOS grid.

$$\text{POCP} = \frac{\frac{a}{b}}{\frac{c}{d}} \times 100$$

where (a) - Change in photochemical oxidant formation due to a change in a VOC emission
(b) - Integrated VOC emission up to that time
(c) - Change in photochemical oxidant formation due to a change in ethylene emissions
(d) -Integrated ethylene emission up to that time

It is a quantity derived from a photochemical ozone model by following the photochemical ozone production with and without the presence of an individual hydrocarbon. The difference in ozone concentrations between such pairs of model calculations is a measure of the contribution that VOC makes in ozone formation.

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# Appendix B Comments on Table 4 by Derwent

**Department of the Environment**
Room B358
Romney House 43 Marsham Street London SW1P 3PY
Telex 22221
Direct Line 071-276 8881
Switchboard 071-276 3000
GTN 276

Professor Peter Builtjes
TNO Institute of Environmental Sciences
PO Box 6011
2600 JA Delft
The Netherlands

**FAX**

27 March 1992

Dear Peter

**The POCPs of Oxygenated Solvents**

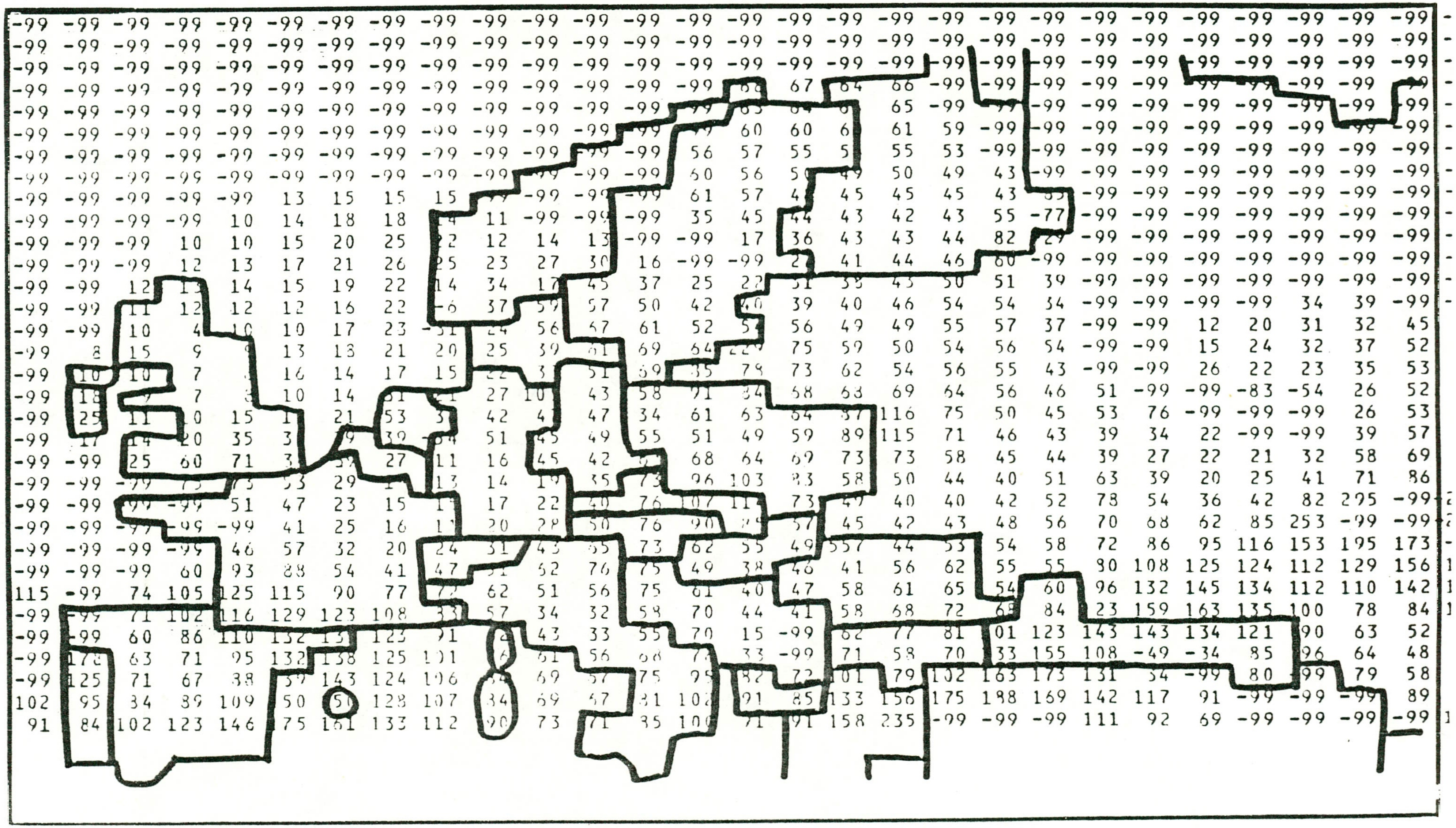
Many thanks for showing me your fascinating table of POCPs. You seem to have done an excellent job and I really have few problems with your assignments. In due course we hope to commission laboratory kinetic studies of OH rate coefficients for newly discovered VOCs. You may wish to note that Professor Mike Pilling, Environment Centre and School of Chemistry. The University, Leeds LS2 9JT has taken over our Department's interest in POCPs. He has employed a range of evaluation techniques to estimate OH rate coefficients and hence POCPs for a wide range of hydrocarbons. You may wish to consult him directly on +532 336451 (telephone) +532 336565 (fax).

On page 18 of your report you list a few hydrocarbons with "unknown" POCPs. This is a little bit of a challenge. I note that "butanoic acid, 3-oxo, ethyl ester" is also listed on your page 17 and given a POCP of 20. This seems about right to me. For the substituted ethanols, I would give them a POCP of 30 by comparison with propylene glycol.

I would strongly recommend that you try and make contact with Professor Mike Pilling, if you can.

All the best.

pp Mrs P. Turner
R G Derwent
AQ Science Unit



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)0 ÷ ( 03(base-run )-03(n-butane ) ) / ( 03(base-run )-03(ethylene ) )          time = 850714 hour=15
   2   3   4   5   6   7   8   9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29
 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99
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 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 [illegible] 67  64  66 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99
 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 [illegible] [illegible] [illegible] 65 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99
 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99  60  60 [illegible] 61  59 -99 -99 -99 -99 -99 -99 -99 -99 -99
 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99  56  57  55 [illegible] 55  53 -99 -99 -99 -99 -99 -99 -99 -99 -99
 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99 -99  60  56 [illegible] 49  50  49  43 -99 -99 -99 -99 -99 -99 -99 -99
 -99 -99 -99 -99 -99  13  15  15  15 -99 -99 -99 -99  61  57 [illegible] 45  45  45  43 [illegible] -99 -99 -99 -99 -99 -99 -99
 -99 -99 -99 -99  10  14  18  18 [illegible] 11 -99 -99 -99  35  45  44  43  42  43  55 -77 -99 -99 -99 -99 -99 -99 -99
 -99 -99 -99  10  10  15  20  25  22  12  14  13 -99 -99  17  36  43  43  44  82 [illegible] -99 -99 -99 -99 -99 -99 -99
 -99 -99 -99  12  13  17  21  26  25  23  27  30  16 -99 -99 [illegible] 41  44  46  60 -99 -99 -99 -99 -99 -99 -99 -99
 -99 -99  12  13  14  15  19  22  14  34  17  45  37  25  22  31  33  43  50  51  39 -99 -99 -99 -99 -99 -99 -99
 -99 -99  11  12  12  12  16  22  -6  37  59  57  50  42  40  39  40  46  54  54  34 -99 -99 -99 -99  34  39 -99
 -99 -99  10   4  10  10  17  23 -31  24  56  67  61  52  54  56  49  49  55  57  37 -99 -99  12  20  31  32  45
 -99   8  15   9   9  13  13  21  20  25  39  61  69  64  22  75  59  50  54  56  54 -99 -99  15  24  32  37  52
 -99  10  10   7 [illegible] 16  14  17  15  22  31  51  69  35  78  73  62  54  56  55  43 -99 -99  26  22  23  35  53
 -99  18 [illegible] 7   3  10  14  51  21  27  10  43  58  71  34  68  63  69  64  56  46  51 -99 -99 -83 -54  26  52
 -99  25  11  10  15 [illegible] 21  53 [illegible] 42 [illegible] 47  34  61  63  64  37 116  75  50  45  53  76 -99 -99 -99  26  53
 -99  17  14  20  35 [illegible] [illegible] 39 [illegible] 51  45  49  55  51  49  59  89 115  71  46  43  39  34  22 -99 -99  39  57
 -99 -99  25  60  71 [illegible] [illegible] 27  11  16  45  42 [illegible] 68  64  69  73  73  58  45  44  39  27  22  21  32  58  69
 -99 -99 -99 [illegible] 73  53  29 [illegible] 13  14  19  35  73  96 103  83  58  50  44  40  51  63  39  20  25  41  71  86
 -99 -99 -99 -99  51  47  23  15 [illegible] 17  22  40  76 107 [illegible] 73  47  40  40  42  52  78  54  36  42  82 295 -99
 -99 -99 -99 -99 -99  41  25  16 [illegible] 20  28  50  76  90 [illegible] 57  45  42  43  48  56  70  68  62  85 253 -99 -99
 -99 -99 -99 -99  46  57  32  20  24  31  43  55  73  62  55  49  57  44  53  54  58  72  86  95 116 153 195 173
 -99 -99 -99  60  93  88  54  41  47  51  62  76  75  49  38  46  41  56  62  55  55  80 108 125 124 112 129 156
 115 -99  74 105 125 115  90  77  72  62  51  56  75  61  40  47  58  61  65  54  60  96 132 145 134 112 110 142
 -99 -99  71 102 116 129 123 108  33  57  34  32  58  70  44  41  58  68  72  68  84 123 159 163 135 100  78  84
 -99 -99  60  86 110 132 [illegible] 123  91 [illegible] 43  33  55  70  15 -99  62  77  81 101 123 143 143 134 121  90  63  52
 -99 172  63  71  95 132 138 125 101 [illegible] 61  56  68 [illegible] 33 -99  71  58  70 133 155 108 -49 -34  85  96  64  48
 -99 125  71  67  38 [illegible] 143 124 106 [illegible] 69  57  75  95  82  72 101  79 102 163 173 131  54 -99  80  99  79  58
 102  95  34  39 109  50  50 128 107  34  69  67  81 102  91  85 133 156 175 198 169 142 117  91 -99 -99 -99  89
  91  84 102 123 146 175 161 133 112  90  73  71  35 100  71  91 158 235 -99 -99 -99 111  92  69 -99 -99 -99 -99
```

FIGURE 1 : LOTOS - POCP results for n-butane

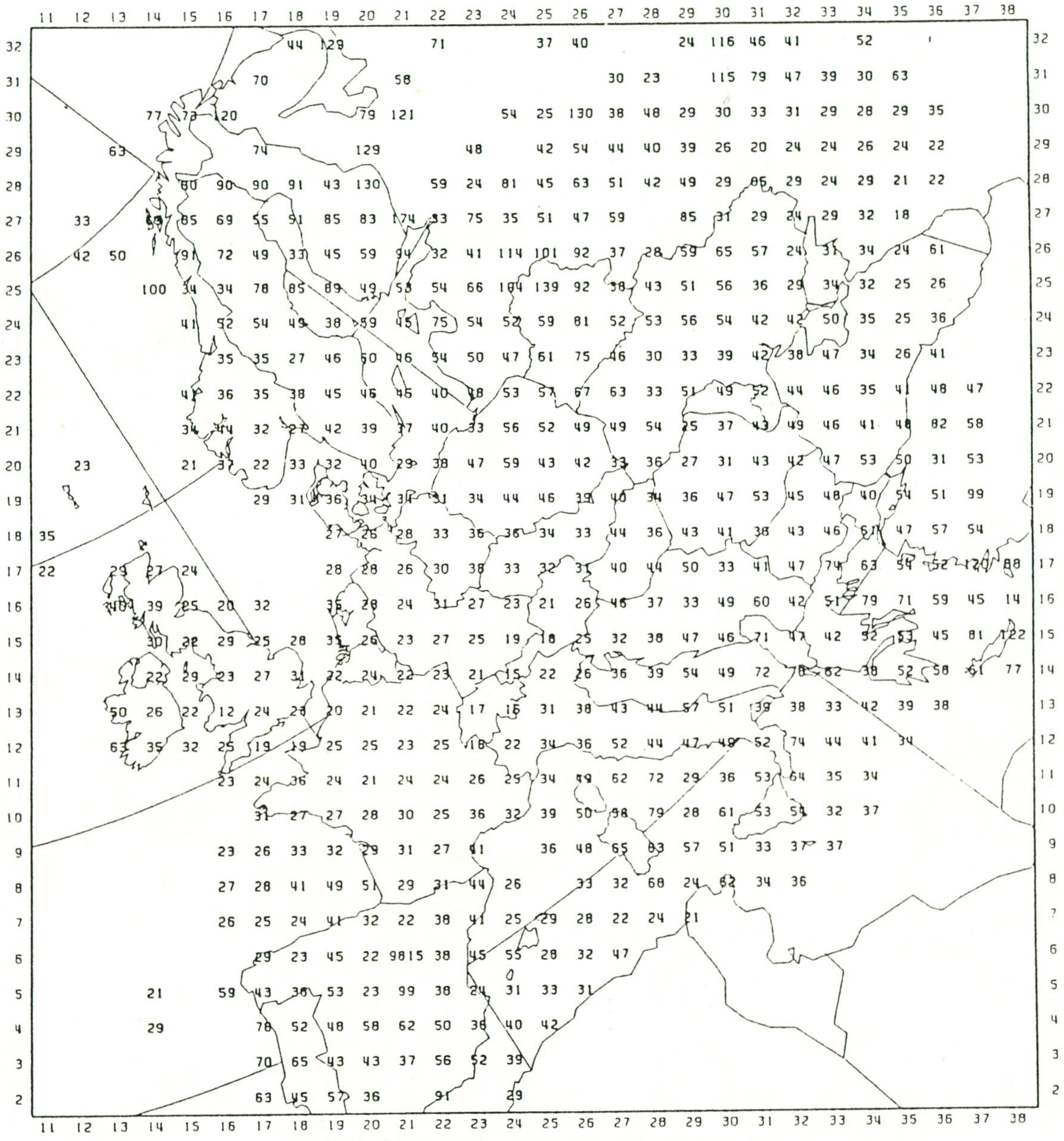

FIGURE 2 : EMEP - POCP results for n-butane