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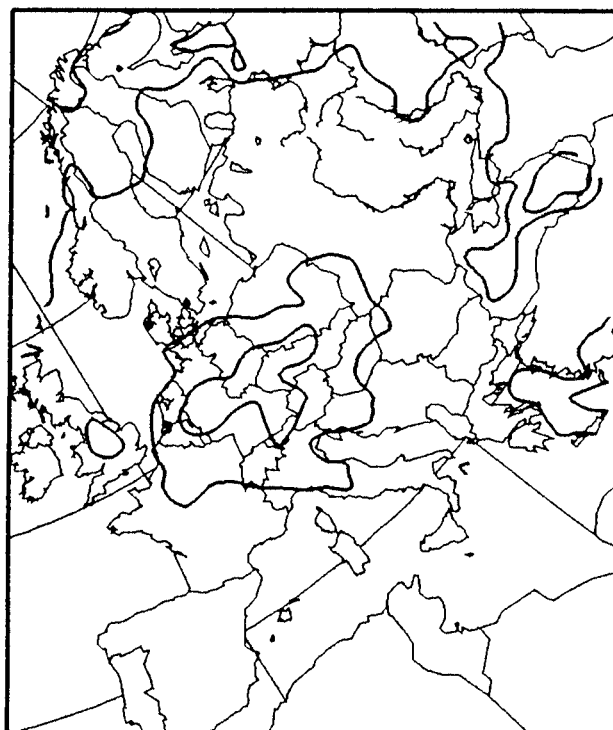
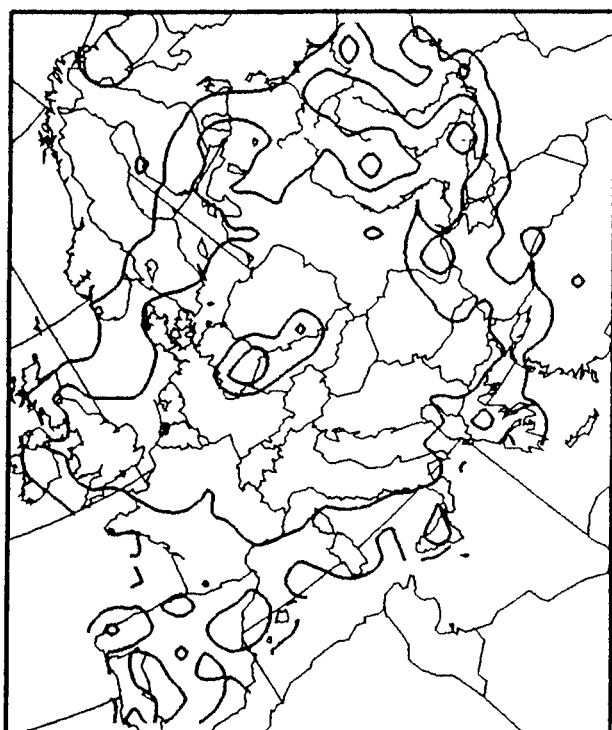
CO-OPERATIVE PROGRAMME FOR MONITORING
AND EVALUATION OF THE LONG RANGE
TRANSMISSION OF AIR POLLUTANTS IN EUROPE

LONG PERIOD MODELLING OF PHOTOCHEMICAL OXIDANTS IN EUROPE:

A) Hydrocarbon reactivity and ozone formation in Europe

B) On the linearity of country-to-country ozone calculations
in Europe.

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PREFACE AND ACKNOWLEDGEMENTS

This note was prepared for the Sixteenth Session of the EMEP Steering Body. Preliminary results from two studies are reported, following up on the two themes covered in EMEP Note 1/91 (Some properties of targeted VOC emission reduction). The two studies are:

A) Hydrocarbon reactivity and ozone formation in Europe. This study, first presented at the EUROTRAC symposium held in Garmisch Partenkirchen in April 1992, looks at the reasons for the variations in photochemical ozone formation potential found in different areas and under different photochemical conditions.

B) On the linearity of country-to-country ozone calculations in Europe. This study attempts to assess the degree of non-linearity in the relationship between NO_x and VOC emissions and formation of ozone over Europe. We show that within certain limits, it is possible to create a blame-matrix for ozone with respect to changes in VOC emissions. Such a blame matrix is presented.

The second study in particular has only just begun, and the results have only been analyzed in an empirical way so far. More theoretical work is required to fully understand the results, and model experiments are required to assess the interactions between NO_x and VOC emissions from different countries.

Thanks are due to Helge Styve of the Norwegian Meteorological Institute for organising the emissions data. Valuable discussions with Dr. R.G. Derwent (U.K. Dept. of the Environment) and Prof. Ø. Hov (University of Bergen, Norway) are appreciated.

The routine activities at MSC-W strongly depend on access to high quality meteorological data. These data are provided by the routine Numerical Weather Prediction model at the Norwegian Meteorological Institute.

The calculations presented in this report have been made possible by access to the CRAY Y-MP4D/464 supercomputer at the Norwegian Technical University (SIMa), Trondheim, Norway.

1.1. Introduction

This report describes two sets of studies which use the EMEP MSC-W ozone model to evaluate particular aspects of anthropogenic VOC and NO_x emission control. Both studies follow up on the work described in EMEP Note 1/91 (Simpson, 1991a).

A) Hydrocarbon Reactivity and Ozone Formation in Europe.

This study follows up on the results found in Note 1/91 showing that the photochemical ozone creation potential (POCP, see Derwent & Jenkin, 1991) of a given hydrocarbon varied quite strongly with geographical location, and with the severity of ozone episode which we considered. In the present study, we investigate some of the reasons for these variations in the POCP values, and show that many of these variations can be explained by a consideration of the lifetimes of the individual VOC species and their degradation products.

B) On the Linearity of country-to-country Ozone calculations in Europe.

In Note 1/91 we compared the changes in ozone concentrations over Europe resulting from VOC emission reductions made in 5 different countries over the period of July 1985. This study showed that there were in fact large differences in the effectiveness of VOC control, depending on the geographical area in which it is applied. The results of this study also suggested that for any given country, the amount of ozone reduction produced by a given amount of VOC reduction varied in a reasonably linear way with the amount of VOC reduction. In the present study, we try to extend these results by considering the reasons and limits of this linearity, and show the importance of the NO_x levels for these relationships. We show that within certain limits, a "blame-matrix" for ozone with respect to VOC emissions gives useful information on the relative effectiveness of VOC control in different countries. Such a blame matrix is presented for the summer of 1989.

Both of these studies are only concerned with changes in anthropogenic VOC emissions. Natural (isoprene) emissions are taken into account in the ozone model as discussed in Simpson (1992a). A further study on the importance of natural VOC species will be reported separately (Simpson, 1992b).

Note: throughout this note the term VOC is used to refer to all volatile organic compounds except methane.

Units: throughout this note the units used for ozone are ppb (1ppb = 1 part per billion = 1 molecule of ozone per 10⁹ molecules air) or ppt (1ppt = 1 part per trillion = 1 molecule of ozone per 10¹² molecules air). In mass units, 1 ppb O₃ (by volume) is equal to 2.00 µg m⁻³ O₃ at 20°C and 1013 mb pressure.

1.2. The Model

The EMEP MSC-W oxidant model has been described in detail elsewhere (Simpson, 1992a, 1991b). In many ways it is a combination of the so-called "Norwegian" photochemical oxidant model (Eliassen et al., 1982, Hov et al., 1985) and the EMEP MSC-W acid deposition model (Hov et al., 1987, Iversen, 1990, Sandnes and Styve, 1992). The model is a single layer trajectory model which calculates concentrations of photochemical oxidants every 6 hours for a set of 709 grid squares covering the whole of Europe. The chemical scheme includes about 100 chemical reactions between 45 chemical species. Emissions from both man-made sources (NO, SO₂, CO, and VOCs represented by ethane, ethene, propene, n-butane, o-xylene, and ethanol) and from forests (isoprene) are included. This model has now been applied over two summertime periods : April-September 1985, and April-October 1989 (Simpson, 1991b), and has been shown to give favourable comparisons with measurements of ozone and other species (*ibid.*). The main changes in the current version have been the introduction a seasonal variation to the background (tropospheric) VOC concentrations, some modifications to the nitrogen chemistry, and a more systematic calculation of ozone concentrations over sea areas.

1.3. Emissions

The national emissions data used in the investigation of hydrocarbon reactivity are those given in Simpson (1991b). The most up-to-date figures available by June 1992, and those used in the linearity studies, are given in Table 1.

In addition, the speciation of the input anthropogenic VOC emissions has been altered to reflect the VOC speciation suggested by Derwent and Jenkin (1991). In this new version, the VOC emissions are split as : 7.5% ethane, 12.1% ethanol, 35.9% n-butane, 3.2% ethylene, 4.1% propylene, and 19.5% o-xylene, on a mass by mass basis.

The natural VOC emissions used in the model are estimated continuously (ie. at every time step), using the model's surface temperature data, a forest cover database derived largely from Lubkert & Schöpp (1989), and a set of emission-temperature relationships (*ibid.*). The resulting annual estimates are also given in Table 1.

	SO2	NOX	VOC-M	VOC-N
ALBANIA	25	9	33	16
AUSTRIA	50	211	408	11
BELGIUM	207	317	335	6
BULGARIA	633	156	167	48
CZECHOSLOVAKIA	1282	1122	295	24
DENMARK	96	252	176	1
FINLAND	121	284	162	30
FRANCE	667	1772	1972	126
GERMAN DEMOCRATIC REP.	2621	705	1050	13
GERMANY, FEDERAL REP. OF	501	2707	2536	41
GREECE	250	746	185	46
HUNGARY	542	249	205	33
ICELAND	3	12	8	0
IRELAND	81	127	90	0
ITALY	1203	1755	1642	96
LUXEMBOURG	6	16	13	0
NETHERLANDS	122	551	442	3
NORWAY	30	220	216	7
POLAND	1955	1480	1131	34
PORTUGAL	104	132	149	57
ROMANIA	900	390	386	66
SPAIN	1095	950	897	370
SWEDEN	87	384	460	24
SWITZERLAND	34	183	298	4
TURKEY	199	175	263	204
USSR (EUROPEAN)	4682	4418	9065	1461
UNITED KINGDOM	1850	2690	1986	1
YUGOSLAVIA	775	430	291	152

Table 1. National emissions estimates for 1989 employed in the calculations. VOC-M represents man-made (non-methane) VOC, VOC-N represents natural VOC emissions. Units: 1000 tonnes per annum, SO₂ as S, NO_x as NO₂

2. Hydrocarbon reactivity and ozone formation in Europe

2.1. Introduction

Ozone production in the atmospheric boundary layer is a complex function of both meteorological and chemical factors. The amount of ozone produced by a given hydrocarbon depends not only on the reactivity and degradation pathways of that hydrocarbon, but also on the time-scales available for reactions to occur, the local photolysis rates, ambient temperatures, the competition for OH radicals from other hydrocarbons, the concentrations of NO_x in the air parcel.

Derwent & Jenkin (1991) introduced the a so-called photochemical ozone creation potential (POCP) in order to quantify these differences, where the POCP expresses the ozone forming ability of any VOC relative to that of ethene. Slightly different definitions of POCP have been used by different workers. In the EMEP studies, we use the following definition for the POCP value of a species *i* :

$$\text{POCP}_i = 100 \times \frac{\text{change in (mean or excess) ozone when species } i \text{ reduced}}{\text{change in (mean or excess) ozone when ethene reduced}} \quad (2.1)$$

where the mass emission reduction for both ethene and species *i* are identical. We perform all spatial and temporal averaging on the ozone concentrations before we evaluate the POCP index - this ensures that the POCPs so calculated are directly related to the amount of ozone change involved. (As the denominator in equation (2.1) is variable, evaluating the POCP every day, then averaging, would give POCP values which were harder to interpret). In all POCP studies, the POCP of ethene = 100 by definition.

Studies by several workers (Andersson-Sköld et al., 1991, Derwent & Jenkin, 1991, Simpson, 1991a) have shown that in qualitative terms POCPs can be used to rank VOCs in terms of their importance to ozone formation. However, all studies showed significant variability in the POCPs assigned to each VOC species. This variability was often quite systematic, depending on time along trajectory (Derwent & Jenkin, 1991) or severity of ozone episode (Simpson, 1991a). For example, Table 2, reproduced from Simpson (1991a), shows POCP values calculated for 5 VOC species for those days in which ozone concentrations exceed a given limit value. We see that the POCP values of the less reactive species steadily increase as the ozone episodes become more severe.

In this paper, we describe briefly some of the principles involved in understanding ozone forming potentials of particular hydrocarbons in realistic atmospheric situations. We make use of a complex photochemical oxidant model to quantify how the time-scales for the reaction of emitted hydrocarbons and their oxidation products vary with OH level and time of year, and show that this can explain many of these systematic changes in the POCP values. Finally, we illustrate the difference in ozone formation potentials of one hydrocarbon, n-butane, as a function of spatial location and time of year.

Table 2*. Calculated POCP Values for Modelled Ozone Values in Excess of 60, 75, 100 and 120 ppb.

Ozone Limit Value (ppb)	Ethane	n-butane	Propene	o-xylene	Ethanol
60	8.6	36.1	97.1	73.8	21.8
75	10.6	42.4	98.5	77.5	26.1
100	15.0	53.7	96.2	82.9	34.1
120	16.7	62.2	96.5	88.2	37.1

*(from Simpson, 1991a)

We make use of the EMEP photo-oxidant model as a means of quantifying the complex interactions between the chemistry and meteorology over Europe. One of the most important model outputs in this work, the predicted OH concentrations along trajectories arriving at 3 sites during April - Sept. 1989 are shown in Fig. 1. Although the chosen sites cover a wide geographical and climatic range, we see that the predicted OH concentrations actually follow quite similar patterns, ranging from ca. 1×10^6 molecules cm^{-3} in April and September to ca. 4×10^6 molecules cm^{-3} in peak summer periods. We make use of this result in the following discussions.

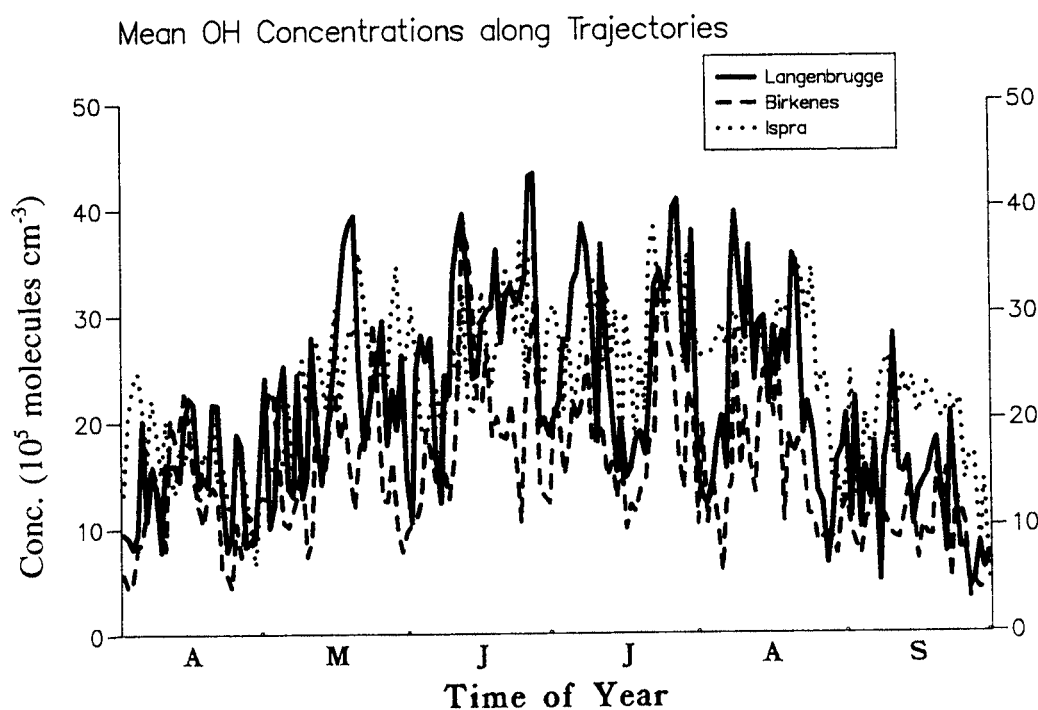
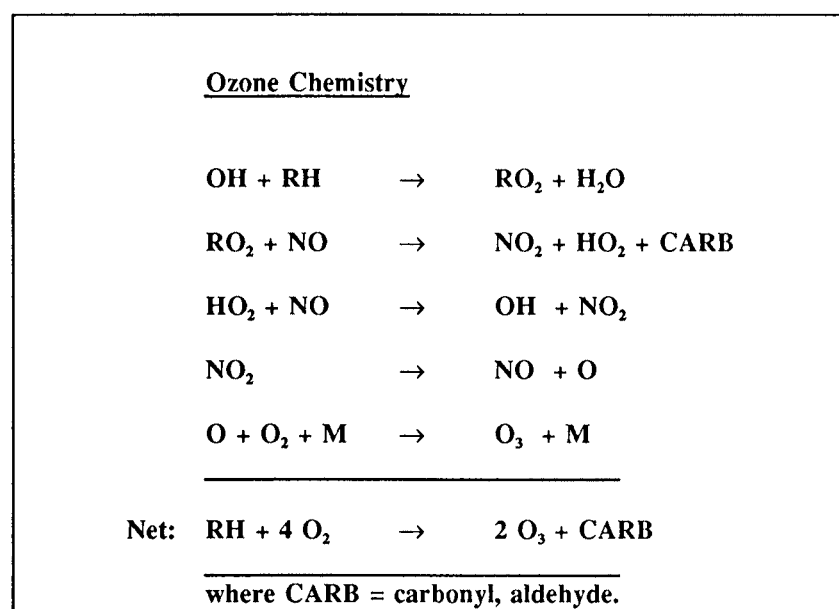


Fig. 1. Calculated concentrations of OH along trajectories arriving at three sites: Birkenes (Norway), Langenbrugge (FRG), and Ispra (Italy). April - Sept. 1989. (Concentrations are the average values over the last 3 days of trajectories).

2.2 Chemistry and time-scales of ozone formation

Many of the basic principles of ozone formation can be deduced from the simple representation shown below, with RH representing the initial hydrocarbon. A useful discussion can be found in Sillman et al. (1990). [N.B. In the remainder of this section we shall confine the discussion to the case of ozone formation in relatively NO_x rich conditions, ie. we shall assume that peroxy radicals (HO_2 , RO_2 , where R could be CH_3 , C_2H_5 , etc.) react primarily with NO to form NO_2 , rather than with other peroxy radicals. At least in the model results, this assumption has been found to hold quite well in nearly all parts of Europe because of the high density of NO_x emissions, especially in N.W. regions.]



This simple scheme suggests that in the presence of NO, the direct attack of OH on the initial hydrocarbon will produce 2 ozone molecules and a carbonyl compound. In reality, some hydrocarbons produce 3 or more O_3 molecules, and often more than one carbonyl product, as illustrated in Table 3, adapted from Warneck (1988). Although not all NO_2 molecules will photolyze to produce O_3 (indeed a substantial proportion can be expected to become involved in PAN or HNO_3 formation), these numbers suggest that for each molecule reacted, larger alkanes might produce much more ozone than the lighter alkenes. However, in practice, the build-up of elevated levels of ozone within the boundary layer can only occur over a limited time-period, usually of ca. 1-4 days duration. Over this time-scale the number of VOC molecules which can react can be severely limited by the rate at which OH-attack occurs, and on the rates at which the intermediate carbonyl compounds enter into further ozone-forming reactions.

Combining the predicted range of OH concentrations ($2\text{--}4 \times 10^6 \text{ molecules cm}^{-3}$) suggested by Fig. 1 with the known OH rate-constants, we can estimate the chemical life-times for typical VOCs species, shown in Table 4.

Table 3. Theoretical chemical potential for ozone formation by several hydrocarbons following their reaction with OH radicals¹. (Adapted from Warneck, 1988).

Compound	Intermediate aldehydes & ketones	Number of NO molecules converted		
		Initial	From carbonyl compounds	Total
Ethene	2 HCHO	2	2	4
Propene	CH ₃ CHO, HCHO	2	5	7
Ethane	CH ₃ CHO	2	4	6
n-Butane	2 CH ₃ CHO	3	8	11

¹ The number of NO molecules converted to NO₂ per hydrocarbon molecule is given for two stages of the oxidation: from the initial stage leading only to the formation of aldehydes and ketones, and the further oxidation of these carbonyl compounds.

Table 4. Timescales for reaction of OH with atmospheric VOCs

VOC class ¹	Example	Lifetime against OH reaction ²	
		(a)	(b)
Methane	CH ₄	413 days	> 2 years
Alkanes (31 %) (non-methane)	Ethane n-butane	12 days 33 h	24 days 66 h
Alkenes (4.2 %)	Ethene Propene	8 h 2-3 h	16 h 5 h
Aromatics (19.5%)	Toluene o-xylene	12 h 6 h	24 h 12 h
Alcohols (11.6%)	Ethanol	70 h	6 days
Biogenic (?????)	Isoprene	1-2 h	3 h

¹ Figures in parentheses give percentage of non-methane emissions, by mass, from Derwent & Jenkin (1991).

² Assumed temperature = 293 K, OH = (a) $4 \times 10^6 \text{ cm}^{-3}$, (b) $2 \times 10^6 \text{ cm}^{-3}$

If we assume that the generation of high ozone levels usually takes place over periods of 1-4 days, we see that species such as ethene, propene or o-xylene will have completely reacted during this time period, so we can expect that each of these species will have produced its 2 initial NO to NO₂ conversions as given in Table 3. On the other hand, only a small fraction of species such as ethane could react over this time scale, so per unit mass emission we should expect ethane to produce much less ozone than ethene. Species such as n-butane have an intermediate position. Close to the emissions source, little n-butane will have reacted, and ozone formation will be dominated by the fast reacting alkene and aromatic species. However, if ozone formation is taking place on time scales of 2-4 days, as is often the case, a substantial part of the n-butane molecules will have time to react, and ozone formation from the initial oxidation stage may become comparable to that of the alkene species.

Considering the fate of the carbonyl compounds produced following the initial OH attack, the monthly average lifetimes of these species, as predicted by the EMEP model, are given in Table 5. The daily variation in the loss rates of HCHO is illustrated in Fig. 2, which shows lifetimes varying between only 3-4 hours during summer episodes to over 10 hours during spring/autumn. Interestingly, the photochemical loss rates (averaged over a 3-day trajectory) are much less variable than the total loss rates, suggesting that differences in OH levels are more important in reducing the lifetimes of these species during episodes than differences in photolysis rates.

During June 1989, the EMEP model predicts the following fates for HCHO and CH₃CHO at a site in NW Europe (Langenbrugge, F.R.G):

<u>HCHO</u>	55 %	$\text{HCHO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$
	23 %	$\text{HCHO} + h\nu \rightarrow \text{H}_2 + \text{CO}_2$
	14 %	$\text{HCHO} + h\nu \rightarrow \text{HCO} + \text{HO}_2$
	0.3 %	$\text{HCHO} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{HCO}$
	8 %	$\text{HCHO} \rightarrow \text{wet scavenged}$
<u>CH₃CHO</u>	97 %	$\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{COO}_2$
	3 %	$\text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_3\text{O}_2 + \text{HO}_2 + \text{CO}$

The HCO radical generated from the HCHO degradation immediately forms HO₂ + CO. On average, we can thus calculate that each HCHO molecule regenerates 0.83 HO₂ radicals which can immediately become involved in further ozone production. During photochemical episodes this proportion should be higher as wet scavenging is less likely.

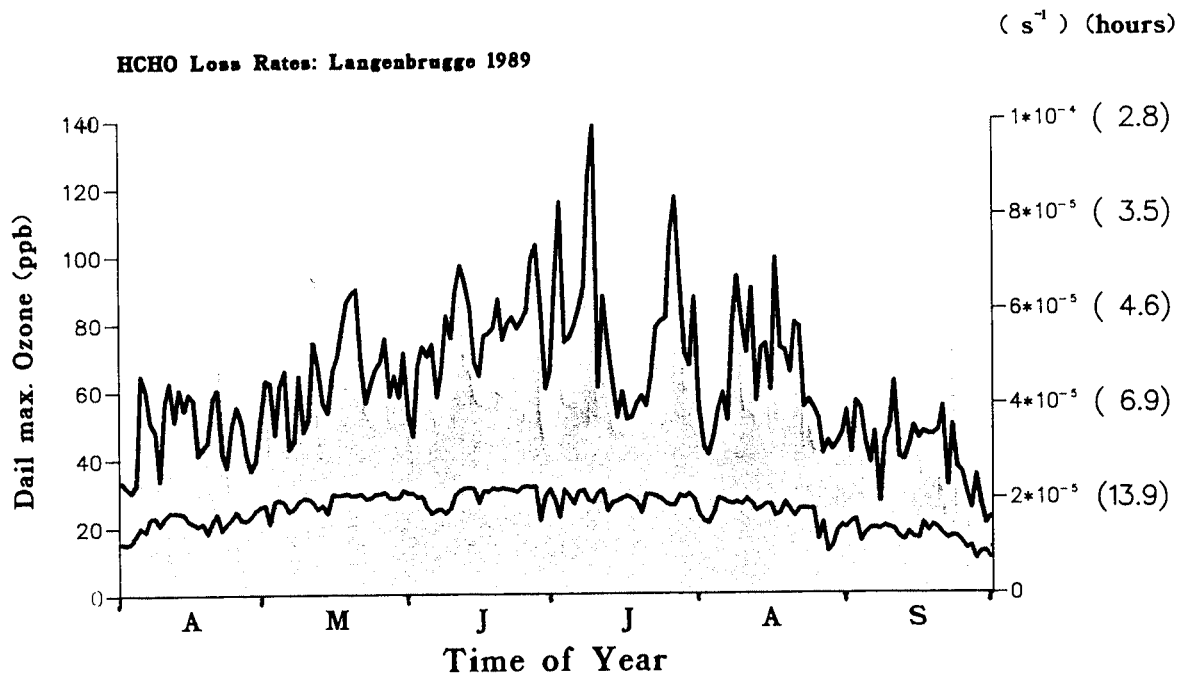
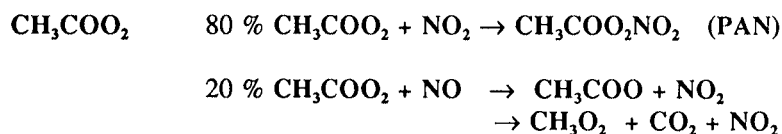


Fig. 2. Predicted loss rates of HCHO (mean along last 72 h of trajectories) for Langenbrugge (FRG), April-Sept. 1989. The upper curve gives the total loss rate, the lower curve gives the loss rate from photolysis. The loss rates in s^{-1} are equivalent to the lifetimes in hours given in the right hand axis in parentheses. Shaded area shows predicted ozone concentrations for comparison.

Table 5. Monthly mean lifetimes (hours) of some key photochemical species. Estimated for Langenbrugge (FRG), 1989, from EMEP MSC-W ozone model.

<u>Month</u>	<u>HCHO</u>	<u>CH₃CHO</u>	<u>PAN</u>
April	8	11	13
May	6	7	8
June	5	6	5
July	5	6	3
August	6	7	3
Sept.	9	12	4

The degradation of the CH_3CHO aldehyde is seen to produce mainly CH_3COO_2 , which reacts as follows:



Thus 20% of the peroxy-acetyl radicals lead to an NO_2 molecule plus the CH_3O_2 radical, but 80% reacts to form PAN. Every time the thermal decomposition of PAN re-releases the CH_3COO_2 molecules, there is an 80% chance of a PAN molecule being reformed, so that PAN effectively locks up the CH_3COO_2 molecules for a time scale significantly greater than the thermal lifetime of PAN itself. As Table 5 shows, the thermal lifetime of PAN varies markedly over the year (depending on temperature), so that the stability or otherwise of this species will play a significant role in determining the ozone forming ability of those VOC species whose chemical degradation leads to CH_3CO radicals (eg. n-butane).

In summary, we should expect species such as ethene which react rapidly with OH, and which generate HCHO, to nearly always attain their maximum ozone forming potentials because the time-scales for both initial hydrocarbon degradation and intermediate-carbonyl degradation are lower than the time-scales available for ozone formation (1-4 days, say). On the other hand, species with moderate OH reactivities, and which generate CH_3CHO rather than HCHO (eg. butane), can be expected to show a wide range of ozone forming potentials, as the time-scales for full chemical degradation may be smaller or larger than the time-scale for ozone formation, depending on temperature, OH levels, and indeed on the ozone forming time scale itself (ie. whether we have 1 day or 4 days). These considerations explain much of the increase in POCP values found with length of trajectory, or with severity of ozone episode, discussed in section 2.1.

2.3 POCP values of n-butane across Europe

In order to illustrate these variations in POCP further, the EMEP MSC-W model has been used to calculate the POCP values of n-butane for April and June, 1989. As illustrated in Fig. 3(a), the POCP values for June show a quite systematic variation. In the region of N.W. Europe covering S.England, N.E. France, Belgium, Netherlands, etc. the POCP values are low: ca. 20-30. This region is that containing the highest VOC emissions, and also the highest ozone concentrations for this month. The POCP values are therefore expected to be low because this close to sources ethene will make a much larger contribution to ozone formation than n-butane. As we move away from this source region (ie. look at longer time-scales) we can expect the POCP values of more slowly reacting VOCs to increase, and this is clearly seen in Fig. 3(a), with POCP values of over 60 in more remote areas.

The corresponding results for April (Fig. 3(b)), show low POCP values (10-20) over nearly the whole of Europe. This again is expected from our previous discussions. The time-scales for reaction of n-butane with OH is long in April (ca. 66 h), and the subsequent ozone forming potential of the CH_3CHO product low because of its long lifetime, and the stability

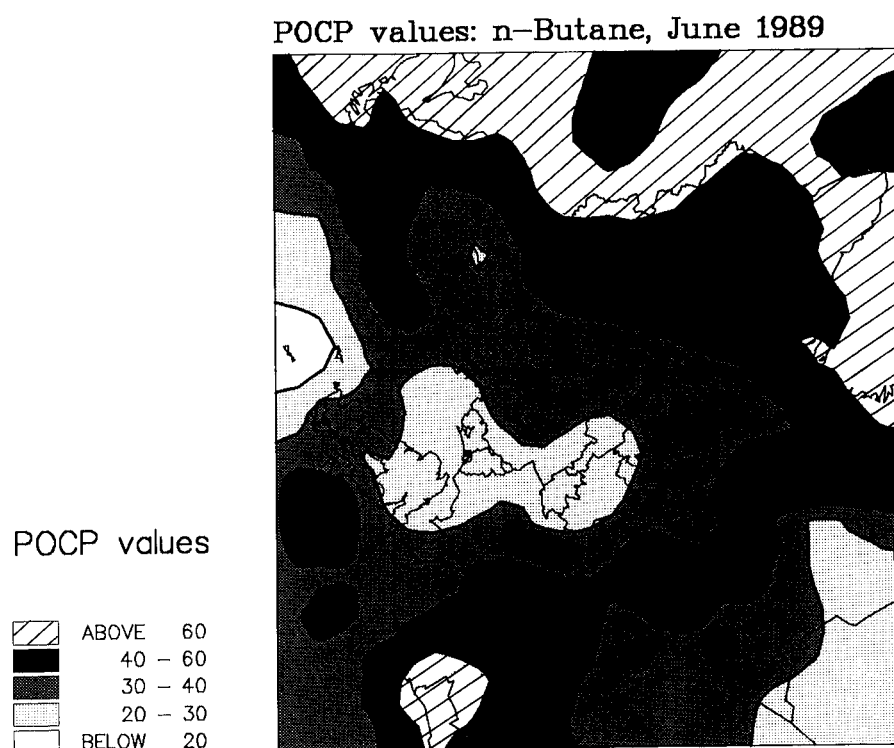


Fig. 3(a). Modelled POCP values for n-butane, June 1989. POCP value = [change in ozone when n-butane reduced x %] / [change in ozone when ethene reduced x %].

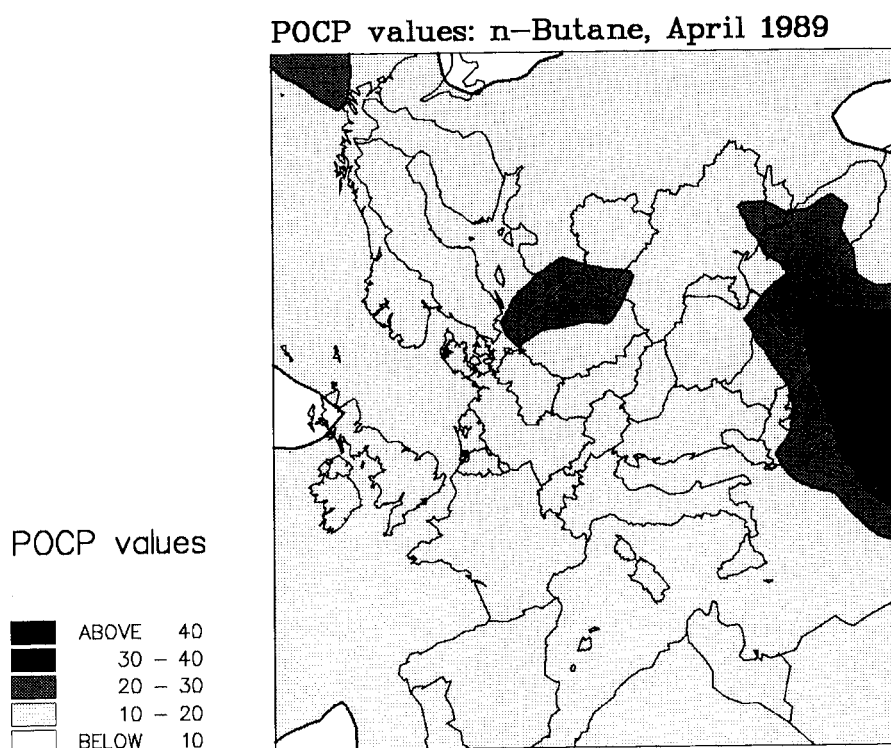


Fig. 3(b). Modelled POCP values for n-butane, April 1989. POCP value = [change in ozone when n-butane reduced x %] / [change in ozone when ethene reduced x %].

of PAN at low temperatures. Thus, even well away from sources, little ozone formation will occur as a result of n-butane oxidation. In contrast, although the chemical degradation of ethene is also slowed down in this month, with lifetimes of ~ 16 h for the initial OH attack, and 8 h for HCHO degradation, these time-scales are still sufficiently short for appreciable ozone formation to take place.

3. On the linearity of country-to-country ozone calculations in Europe.

3.1. Introduction

It is well known that the formation of ozone in a mixture of NO_x and VOCs is a complex, non-linear, function of the concentrations of these precursors. The most obvious example of this is the response of ozone concentrations to NO_x concentrations. At low NO_x concentrations, an increase in NO_x concentrations results in an increase in ozone levels, as a result of the rapid conversion of NO to NO_2 by RO_2 radicals. However, at high NO_x levels, every increase in NO_x concentration actually reduces ozone levels, as a result of the removal of OH and HO_2 radicals by the NO and NO_2 (eg. Warneck, 1988).

However, this non-linearity is not necessarily as strong as is often implied. Indeed, previous calculations with the EMEP MSC-W ozone model (Simpson, 1991a, also unpublished data) have suggested quite a strong linearity if we only consider VOC emissions reductions from one country or area alone. This linearity is expected in conditions where the changes in NO_x and/or VOC have little effect on the concentrations of OH, HO_2 , and other peroxy radicals.

Further, in policy terms, there would be many advantages to the formulation of a "blame-matrix" for ozone, whereby the contribution of VOC or NO_x emissions from one country to ozone formation in other countries could be specified. Such matrices have been one of the most useful outputs of EMEP activities in sulphur and nitrogen modelling (eg. Alcamo et al., 1990). Of course, given the non-linearities, we cannot expect to produce an exact solution to this problem. However, an approximate solution may be sufficient for many purposes, and so this note seeks to explore this possibility.

Some attempts at this problem have been made by other workers. Kleinman and Benkovitz (1987) showed that with an assumption of constant HO_2/NO ratios, a linear model for VOC degradation is possible, and have used this to attribute ozone production in the United States to different source categories and VOC species (Benkovitz and Kleinman, 1990). Similarly, Stedman and Williams (1992) have used an even simpler model with some success to model ozone formation over Europe, allocating ozone formation to national VOC emissions.

3.2 The "country to country" model

In order to produce fields of ozone concentrations over Europe, the EMEP ozone model is usually run to the set of 709 grid points covering this area. One month's simulation requires about 40 minutes CPU time on a CRAY Y/MP supercomputer. For the purposes of this study we have modified the model in such a way that if we are interested in the effect of an area (or country) "A" on ozone levels, we re-run for only those trajectories passing over the emission source area "A". One slight disadvantage of this method is that we no longer produce full fields of ozone concentrations across Europe, so we cannot use the assimilation procedure which normally allows us to track concentrations over periods of more than 4 days (see Simpson, 1992a). Instead, initial concentrations at the start of a 4 day run are taken from the results of the base-run. However, this method greatly reduces the computer time needed to assess country specific emission scenarios. For example, we can assess the contribution of a small country's emissions to the rest of Europe using about 5 minutes computing per month.

3.3 Statistics used

In considering the effect of NO_x and VOC emission scenarios on ozone concentrations over Europe, two statistics are used to characterise the resulting changes:

Mean ozone: Monthly mean ozone is used as a measure of the effect of emission reductions on long term ozone concentrations over the 6 months. (To be exact, the monthly average of the daily maximum ozone is used).

Excess ozone In order to take into account the frequency as well as the magnitude of elevated ozone concentrations for a particular grid square or area we have used the statistic "excess ozone". For an ozone limit of 75 ppb this is defined as "Excess ozone" = the sum over all hours in a given time period (eg. month, season) of all ozone concentrations in excess of 75 ppb, ie. :

$$Excess\ ozone = \int_{t=0}^{t=T} \max(C-75.0, 0) dt$$

$$where \max(x, 0) = x \quad \text{if } x > 0; \quad \max(x, 0) = 0 \quad \text{if } x < 0$$

We have used these statistics previously in evaluating the effect of VOC emission reductions in Europe (Simpson, 1991a,b).

Results are generally given as an average per grid square, either over the receiver country concerned, or calculated over all of the European land grid squares in the model area.

Further, in order to make the results of different levels of emission control easier to compare,

we have generally produced tables in which the changes in ozone have been scaled by the emission reduction which has taken place. Thus, using the UK as an example, 30% of the national VOC emission corresponds to ca. 596 ktonnes VOC emission, so we have divided changes in ozone resulting from a 30% VOC reduction in the UK by 596 to get an ozone reduction in terms of ppt per ktonne reduced.

3.4 Calculations for April-September 1989

The mean ozone concentrations calculated across the EMEP area for April-September 1989 in the base case are shown in Figure 4. Despite some changes in emission estimates and model parameters, these results are very similar to those obtained previously for the summer of 1989. The results obtained for excess ozone (not shown) are correspondingly similar.

Before considering the effects of an individual country's emissions on ozone formation, it is worth summarising the predicted sensitivity of ozone in Europe to general changes in NO_x and VOC emissions. Spatial maps of the reductions in 6-monthly mean ozone concentrations obtained in each grid square under 50% NO_x and VOC emission reductions have been presented in Simpson (1991b). These data clearly showed that VOC control was most effective in reducing ozone concentrations in areas around N.W. Europe (Germany/France), whereas NO_x emission control was most effective away from this area.

These spatial dependencies can be interpreted in terms of the high NO_x emission densities found in parts of north-western Europe. In figures 5(a),(b) the same data on ozone reductions as a result of VOC and NO_x emission control are plotted against the mean NO_x concentrations (from the base-case calculation) in each grid square. We see a straightforward relationship between the amount of ozone reduction produced by VOC emission control and the NO_x concentration in the trajectory. The corresponding figure for a 50% reduction in NO_x emissions is much more complex. As expected, at high NO_x concentrations, NO_x emission reduction leads to an increase in ozone, whereas at low NO_x concentrations, NO_x emission reduction does lead to ozone decreases.

3.5 Effects of VOC emission reductions in 5 countries

3.5.1 At 1989 NO_x Emissions levels

The model has been re-run over the April-Sept. 1989 period with the VOC emissions of each of 5 example countries reduced in turn by a fixed percentage. As in Simpson (1991a), the example countries are : Hungary, Norway, Poland, Spain, and the United Kingdom. Three levels of VOC emission reduction were calculated for each country: 10 %, 30 % and 50%. In each case, the emissions of VOC from the remaining (non-emitter) country were kept at 1989 levels (cf. Table 1). The emissions of NO_x from all countries were also kept at 1989 levels.

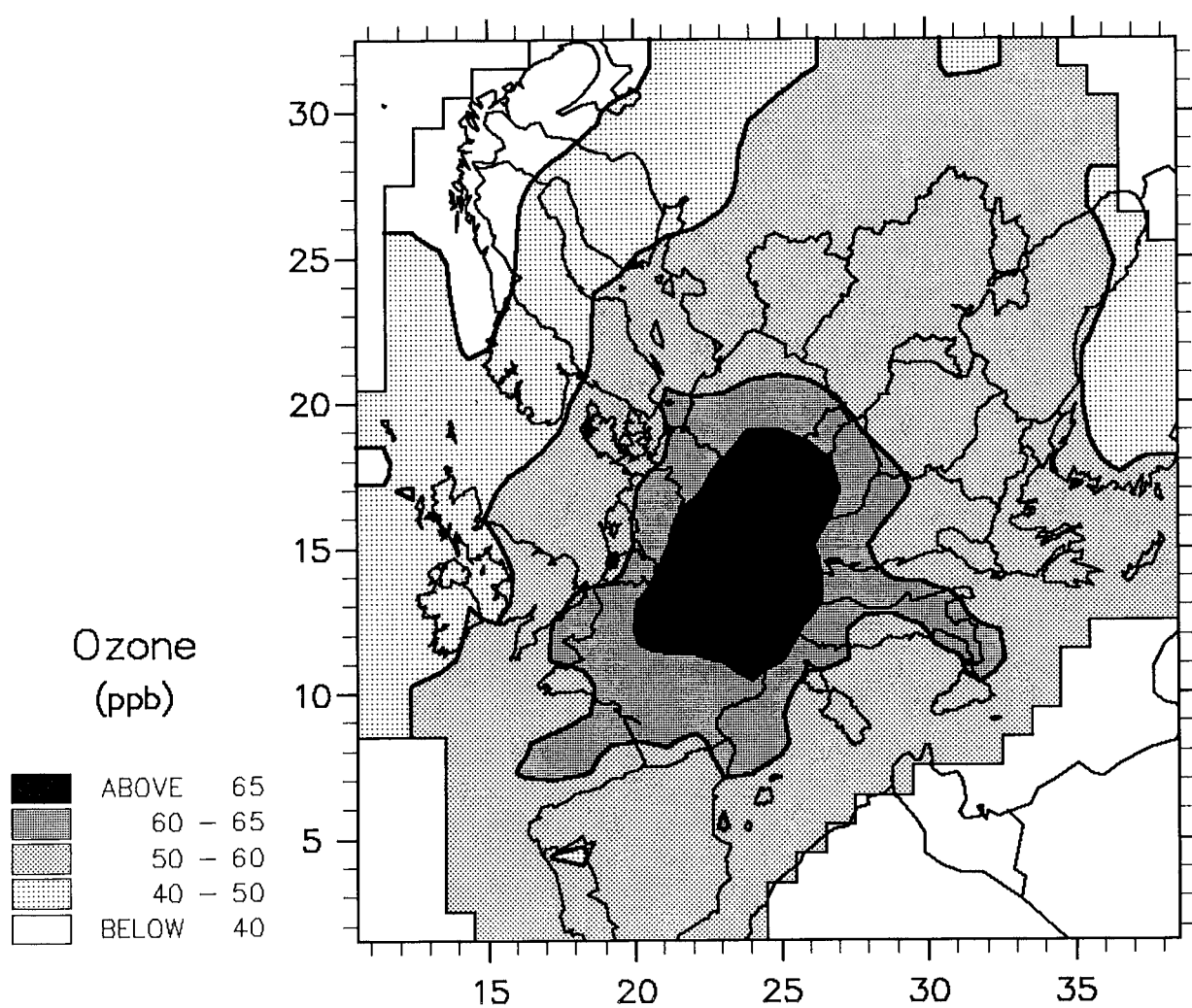


Figure 4. Mean of daily maximum ozone concentrations calculated in the base case. April-September 1989. Units: ppb.

Effect of VOC reductions on ozone. April-Sept 1989

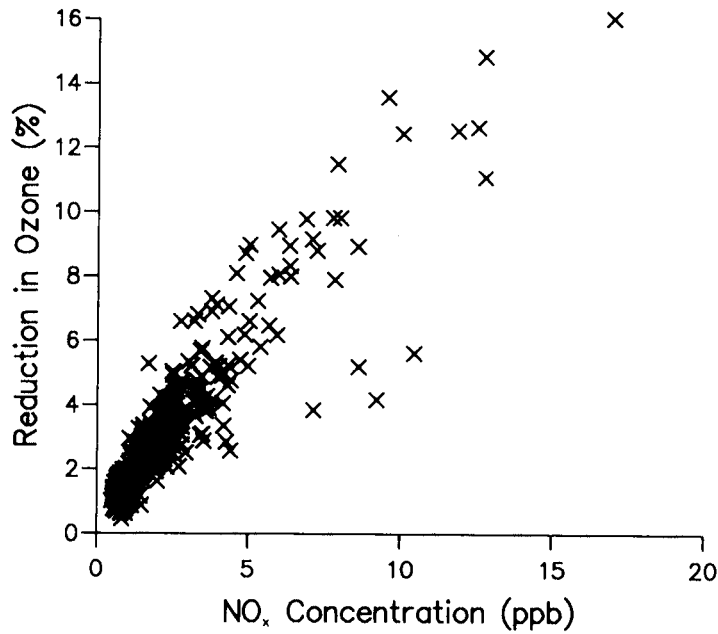


Fig. 5(a). Reductions in mean ozone concentration in each of 709 grid squares as a result of a 50 % VOC emission reduction, plotted against (base-case) NO_x concentrations in each grid square.

Effect of NO_x reductions on ozone. April-Sept 1989

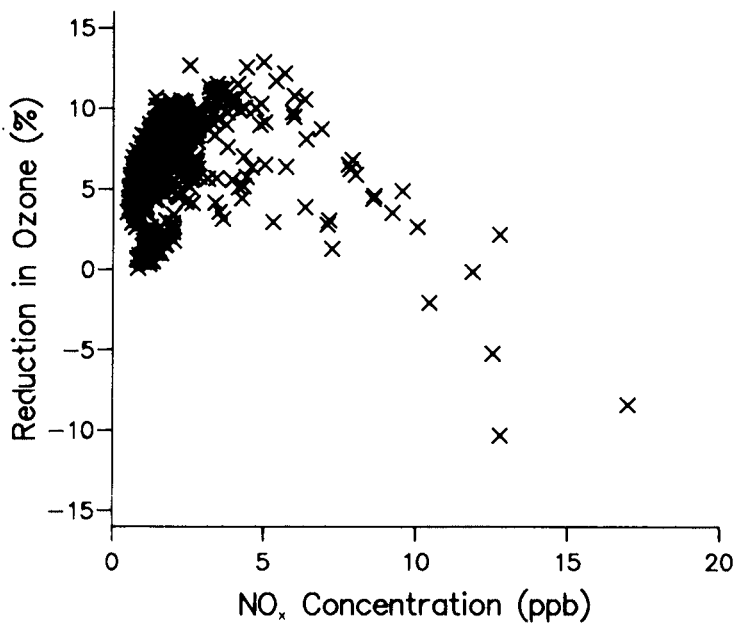


Fig. 5(a). Reductions in mean ozone concentration in each of 709 grid squares as a result of a 50 % NO_x emission reduction, plotted against (base-case) NO_x concentrations in each grid square.

The reductions in 6-monthly mean and excess ozone resulting from the 30 % VOC reduction scenarios are summarised in Table 6(a). Table 6(b) shows the same results after scaling to produce ozone changes per unit (1 ktonne) VOC emission reduced (see section 3.3). These results clearly show that even after accounting for the magnitude of the VOC emissions from each country, there are significant differences in the effectiveness of VOC emission control, depending on the area controlled. For example, as found for the previous July 1985 calculations (Simpson, 1991a), a reduction in a given mass of VOC emissions in the UK produces much greater changes in ozone in Europe than the same mass reduction in Norway.

Table 6(a) Effect of 30 % VOC Emission Reductions on
6-Monthly Mean Ozone and Ozone Excess.
(average per grid square, over European land areas)

Country with Reduced Emissions	Reduction in Monthly Mean Ozone Conc. (ppt)	Reduction in 6-Monthly Excess Ozone (ppb.hours)
Hungary	5.0	2.69
Norway	1.9	0.25
Poland	33.3	7.79
Spain	11.4	2.18
UK	80.3	11.94

Table 6(b) Effect of 30 % VOC Emission Reduction on Monthly Mean
Ozone and Ozone Excess, per unit VOC emission reduced¹.
(average per grid square, over European land areas)

Country with Reduced Emissions	Reduction in Monthly Mean Ozone Conc. (ppt)	Reduction in 6-Monthly Excess Ozone (ppt.hours)
Hungary	0.08	43.69
Norway	0.03	3.85
Poland	0.10	22.97
Spain	0.04	8.11
UK	0.13	20.04

¹ ie. per ktonne VOC reduced

The spatial distributions of these changes in mean and excess ozone resulting from emissions reduction in Hungary, Norway and the UK are shown in Figures 6-8.

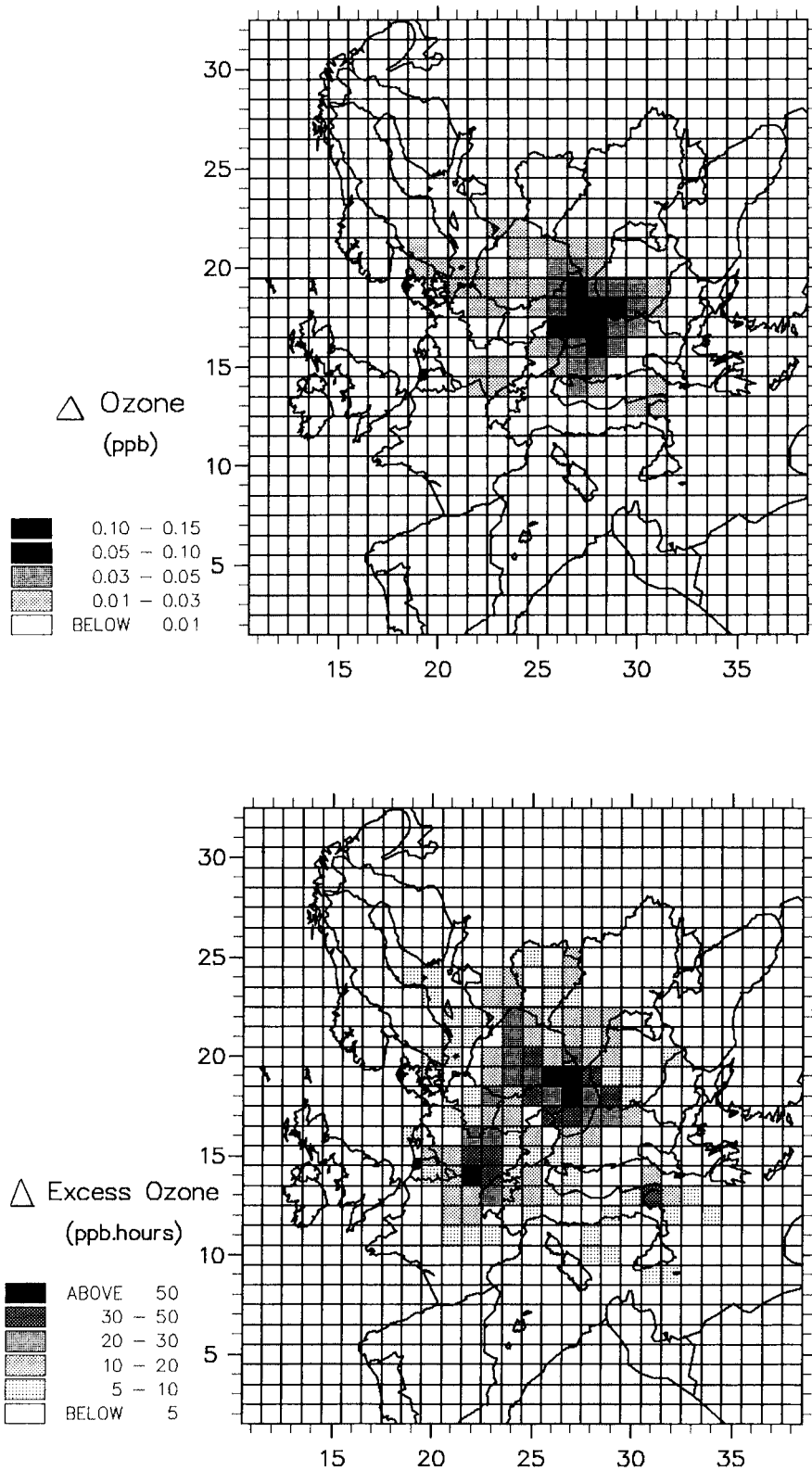


Figure 6. Reductions in mean ozone (top) and excess ozone (bottom) as a result of a 30% reduction in VOC emissions from Hungary. April - Sept. 1989.

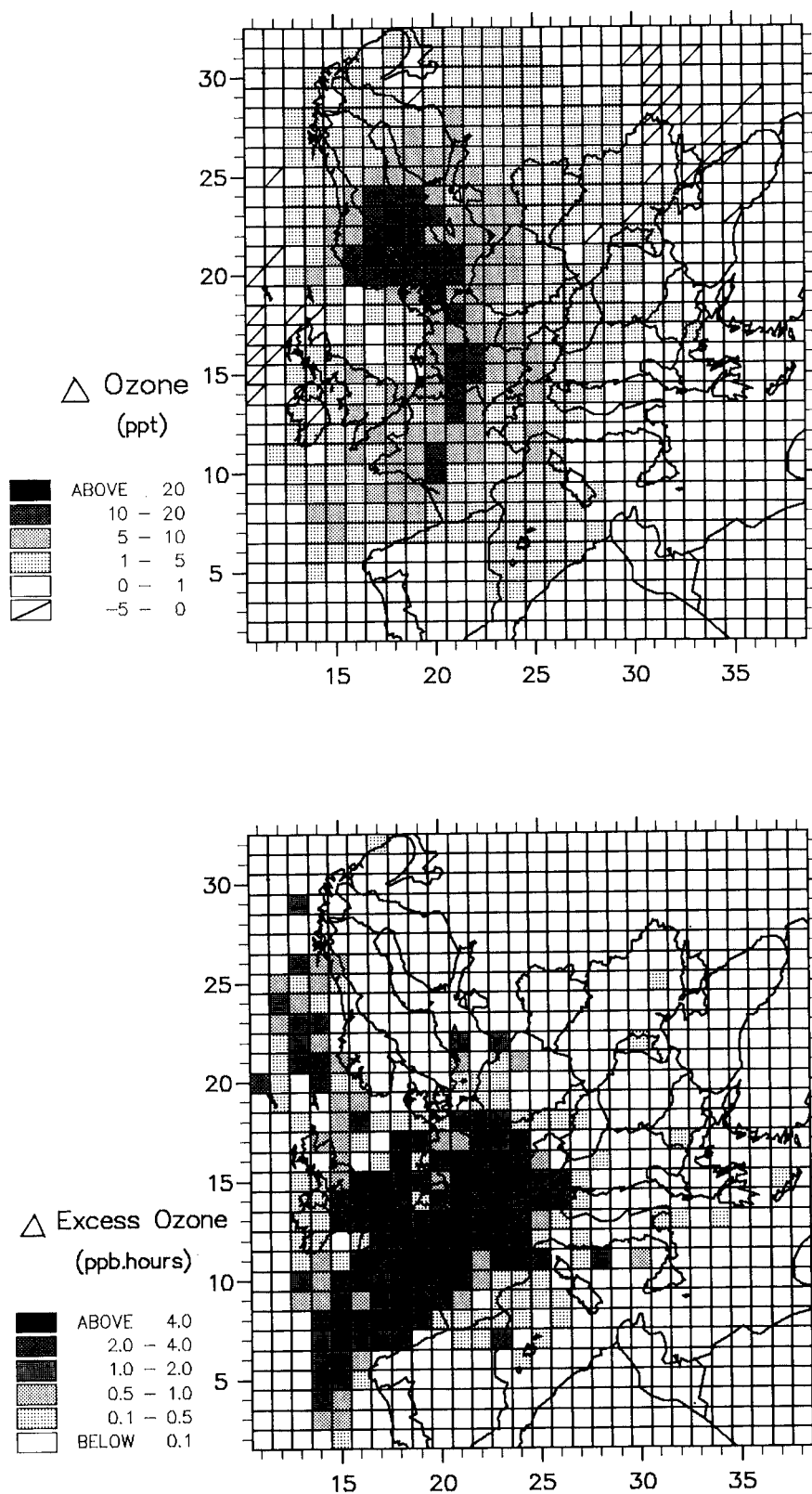


Figure 7. Reductions in mean ozone (top) and excess ozone (bottom) as a result of a 30% reduction in VOC emissions from Norway. April - Sept. 1989.

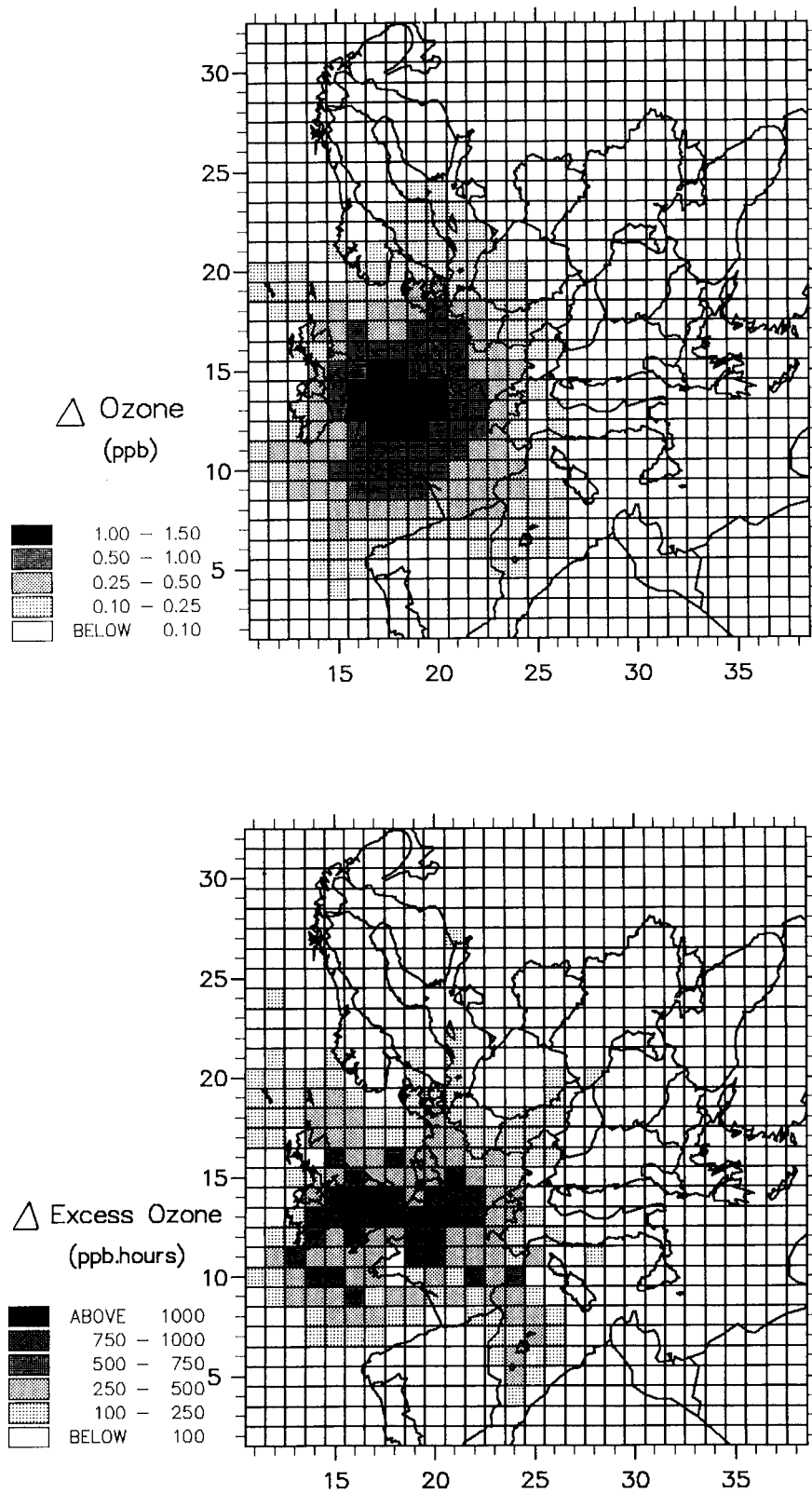


Figure 8. Reductions in mean ozone (top) and excess ozone (bottom) as a result of a 30% reduction in VOC emissions from the UK. April - Sept. 1989.

These results show that for a 1 ktonne reduction in VOC emissions we might expect significantly more ozone reduction from sources in the Hungary, Poland, and the UK than from Norway or Spain. The reasons for this involve a mixture of chemical, meteorological and geographical factors. Chemistry determines the sensitivity of ozone to VOC concentrations in regions of different NO_x concentration, as discussed in section 3.4. Meteorology determines some of the chemical parameters (the lifetime of PAN, for example), but most importantly the frequency with which a particular country can contribute at all. For example, air masses travelling over Norway will often not pass over the more central parts of Europe, so Norwegian VOC emissions often can't contribute significantly to ozone formation. The low contribution of Spanish VOC emissions probably has several explanations. As with Norway, Spain lies near one boundary of the model region, and so its VOC emissions will often not reach other countries. Further, during the summer months, the Iberian peninsula often sees the development of a large scale thermal low system, which gives a convergence of air masses in towards the centre of the peninsula, thus minimising long-range transport to other countries, at least within the boundary layer (Millán et al., 1991). Finally, during the main summer months, the natural isoprene emissions from Spain are currently estimated to be significantly greater than the anthropogenic VOC emissions (Simpson, 1991b), so anthropogenic VOC control can have only limited effect.

The effects of 10, 30, and 50 % reductions in VOC emissions in our example countries on mean ozone in all countries are shown in Tables 7(a)-(c), where now all ozone changes are given per unit VOC reduced. The most striking feature of these tables is that despite the level of VOC emission reduction, the changes in mean ozone per unit VOC are almost identical in all cases. The extent of this linearity is further illustrated in Figure 9(a)-(c) which compares the mean changes in ozone occurring in each grid square as a result of 10 % VOC reductions with those obtained from the 50 % VOC reduction scenarios, for Spain, the UK, and Norway.

In fact, these results are not too surprising. Preliminary investigations have shown that changes in the VOC emissions from any one country do not have very much effect on the concentrations of OH, HO_2 , or other peroxy radical concentrations along a trajectory. With these concentrations approximately constant, the ozone formation equations outlined in section 2 become linear.

The reductions in excess ozone caused by the VOC reduction scenarios are given in Tables 8(a)-(c). Although in many cases these results are also approximately linear, there are some significant exceptions. Some of this non-linearity arises from the definition of excess ozone itself. For example, a small change in ozone from an average of 76 ppb over an area to 77 ppb would lead to a doubling of the calculated excess ozone - a response which is far out of proportion to the minor change in absolute ozone concentrations. However, this statistic merely reflects the assumptions built into a critical level type approach. If such an approach is maintained for ozone this non-linearity becomes hard to avoid. Fortunately, it seems that the UN-ECE value adopted for critical levels for ozone is likely to be reduced (probably to around 40 ppb, Task Force on Mapping, 1992). Excess ozone calculated for such a low figure would then show many of the same properties as mean ozone.

It is also possible that the non-linearity in the excess ozone arises from non-linearities occurring in periods of elevated ozone production. Time has not yet allowed an investigation of the relative importance of these two sources of non-linearity.

a) Results derived from 10 % VOC emission reduction scenarios

Emitter Country						
		HU	NO	PL	ES	UK
R e c e i v e r C o u n t r y	Albania	0.19	0.01	0.09	0.01	0.01
	Austria	0.38	0.08	0.31	0.02	0.24
	Belgium	0.05	0.13	0.34	0.04	1.56
	Bulgaria	0.26	0.01	0.16	0.00	0.00
	Czech.	0.64	0.07	0.84	0.01	0.22
	Denmark	0.06	0.12	0.18	0.02	0.54
	Finland	0.02	0.06	0.07	0.00	0.10
	France	0.04	0.10	0.13	0.11	0.97
	GDR	0.21	0.09	0.49	0.03	0.51
	FRG	0.14	0.13	0.31	0.04	0.76
	Greece	0.14	0.01	0.06	0.01	0.00
	Hungary	1.27	0.04	0.69	0.01	0.08
	Ireland	0.00	0.00	0.04	0.00	0.54
	Italy	0.20	0.04	0.11	0.04	0.15
	Lux.	0.08	0.25	0.35	0.05	1.15
	Netherl.	0.05	0.05	0.29	0.04	1.36
	Norway	0.02	0.14	0.04	0.00	0.12
	Poland	0.39	0.06	0.79	0.01	0.20
	Portugal	0.00	0.00	0.00	0.97	0.06
	Romania	0.54	0.02	0.30	0.00	0.01
	Spain	0.00	0.01	0.01	0.66	0.14
	Sweden	0.09	0.14	0.15	0.00	0.16
	Switz.	0.12	0.07	0.07	0.07	0.57
	Turkey	0.05	0.00	0.03	0.00	0.00
	USSR	0.06	0.02	0.09	0.00	0.03
	UK	0.01	0.06	0.08	0.01	1.46
	Yugosl.	0.49	0.03	0.23	0.01	0.03
	Mean	0.08	0.03	0.10	0.04	0.13

Table 7(a). Decreases in mean ozone in 27 European countries per unit VOC emissions reduced from 5 emitter countries: Hungary (HU), Norway (NO), Poland (PL), Spain (ES), and the UK. Derived from results of 10% VOC emission reduction scenarios (see note below). The "mean" change is the average over all European land areas. Units: ppt per ktonne VOC reduced.

NB. All changes in ozone are scaled by the amount of VOC emission reduction in each country, to give changes in ppt per ktonne VOC. For example, Hungary has an annual VOC emission of 205 ktonnes. A 10 % reduction in Hungary's VOC emissions leads to a reduction in mean ozone concentrations over Austria of 7.79 ppt. Therefore the change in ozone per unit VOC emission reduced in Hungary is $7.79 \text{ ppt} / (10 \% \times 205 \text{ ktonnes}) = 0.38 \text{ ppt per ktonne}$.

b) Results derived from 30 % VOC emission reduction scenarios

Emitter Country						
		HU	NO	PL	ES	UK
R e c e i v e r C o u n t r y	Albania	0.19	0.01	0.10	0.01	0.01
	Austria	0.37	0.07	0.32	0.02	0.25
	Belgium	0.05	0.13	0.35	0.04	1.56
	Bulgaria	0.26	0.01	0.16	0.00	0.00
	Czech.	0.63	0.06	0.86	0.01	0.22
	Denmark	0.06	0.13	0.18	0.02	0.55
	Finland	0.02	0.06	0.07	0.00	0.10
	France	0.04	0.10	0.13	0.12	1.01
	GDR	0.20	0.12	0.50	0.03	0.51
	FRG	0.14	0.13	0.32	0.04	0.77
	Greece	0.14	0.01	0.07	0.01	0.00
	Hungary	1.27	0.04	0.72	0.01	0.08
	Ireland	0.00	0.02	0.04	0.00	0.55
	Italy	0.20	0.04	0.12	0.05	0.15
	Lux.	0.07	0.22	0.36	0.05	1.20
	Netherl.	0.05	0.07	0.30	0.04	1.35
	Norway	0.02	0.14	0.04	0.00	0.12
	Poland	0.39	0.08	0.80	0.01	0.21
	Portugal	0.00	0.00	0.00	0.96	0.06
	Romania	0.54	0.02	0.31	0.00	0.01
	Spain	0.00	0.01	0.01	0.67	0.14
	Sweden	0.09	0.14	0.15	0.00	0.16
	Switz.	0.12	0.06	0.07	0.07	0.60
	Turkey	0.05	0.00	0.03	0.00	0.00
	USSR	0.06	0.02	0.09	0.00	0.03
	UK	0.01	0.05	0.08	0.01	1.44
	Yugosl.	0.49	0.03	0.24	0.01	0.03
Mean		0.08	0.03	0.10	0.04	0.13

Table 7(b). Decreases in mean ozone in 27 European countries per unit VOC emissions reduced from 5 emitter countries. Derived from results of 30% VOC emission reduction scenarios (see notes in Table 7(a)).

c) Results derived from 50 % VOC emission reduction scenarios

Emitter Country						
R e c e i v e r C o u n t r y		HU	NO	PL	ES	UK
	Albania	0.19	0.01	0.10	0.01	0.01
	Austria	0.38	0.07	0.33	0.02	0.25
	Belgium	0.05	0.13	0.36	0.04	1.54
	Bulgaria	0.26	0.01	0.17	0.00	0.00
	Czech.	0.64	0.06	0.89	0.01	0.23
	Denmark	0.06	0.13	0.18	0.02	0.55
	Finland	0.02	0.06	0.07	0.00	0.10
	France	0.04	0.10	0.13	0.12	1.03
	GDR	0.21	0.12	0.51	0.03	0.52
	FRG	0.14	0.13	0.32	0.04	0.77
	Greece	0.14	0.01	0.07	0.01	0.00
	Hungary	1.28	0.04	0.75	0.01	0.08
	Ireland	0.00	0.02	0.04	0.00	0.56
	Italy	0.20	0.04	0.12	0.05	0.15
	Lux.	0.07	0.22	0.37	0.05	1.17
	Netherl.	0.05	0.06	0.30	0.04	1.34
	Norway	0.02	0.14	0.04	0.00	0.13
	Poland	0.39	0.08	0.82	0.01	0.21
	Portugal	0.00	0.00	0.00	0.97	0.06
	Romania	0.54	0.02	0.32	0.00	0.01
	Spain	0.00	0.01	0.01	0.69	0.14
	Sweden	0.09	0.14	0.15	0.00	0.17
	Switz.	0.12	0.06	0.07	0.07	0.63
	Turkey	0.05	0.00	0.03	0.00	0.00
	USSR	0.06	0.02	0.10	0.00	0.03
	UK	0.01	0.05	0.08	0.01	1.42
	Yugosl.	0.49	0.03	0.24	0.01	0.03
	Mean	0.08	0.03	0.10	0.04	0.14

Table 7(c). Decreases in mean ozone in 27 European countries per unit VOC emissions reduced from 5 emitter countries. Derived from results of 50% VOC emission reduction scenarios (see notes in Table 7(a)).

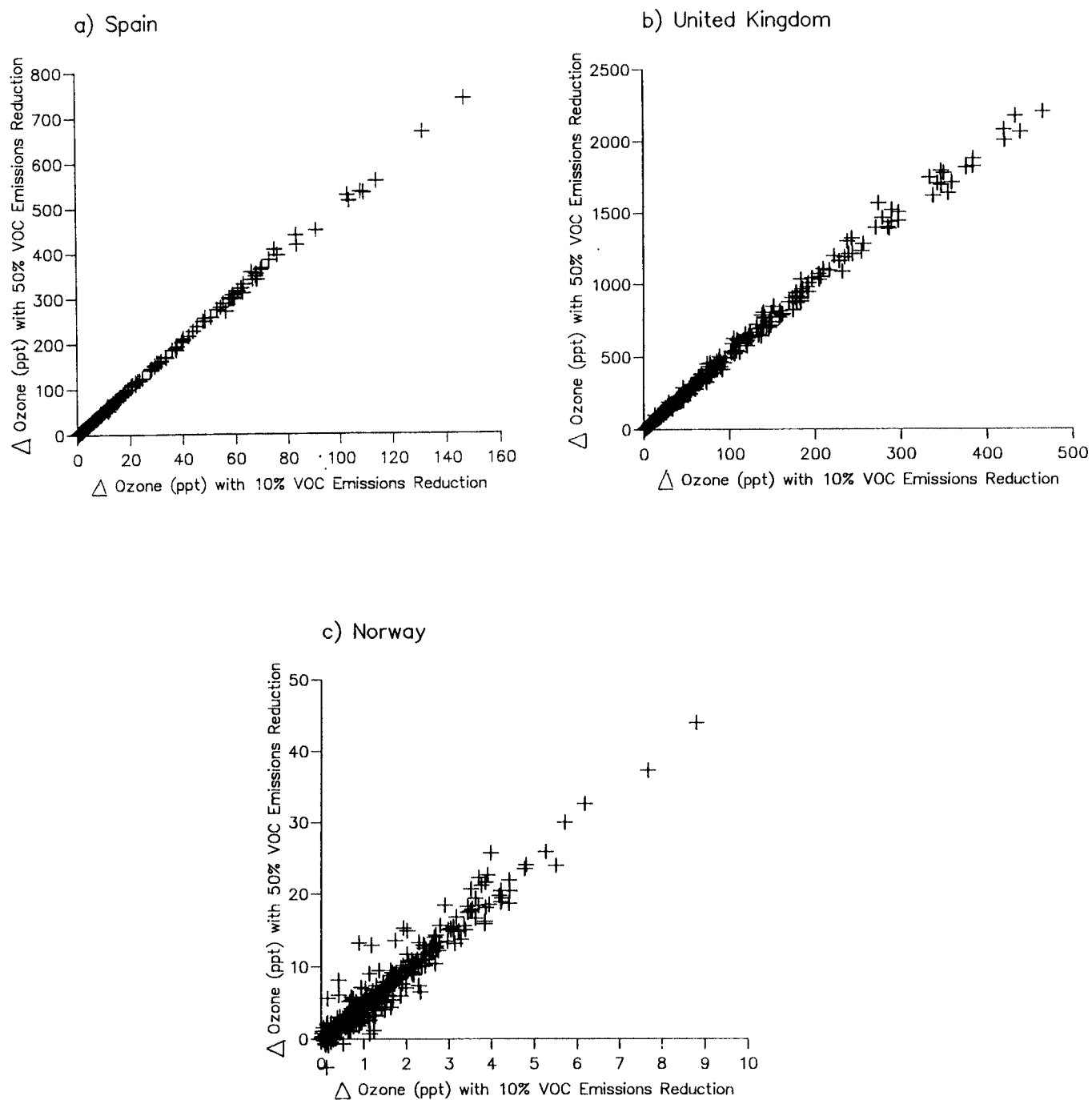


Figure 9. The reductions in mean ozone concentrations in 709 grid squares caused by a 50 % VOC emission control in one country compared with the equivalent ozone reductions caused by 10 % VOC emission control in that country. For VOC emission reductions in (a) Spain, (b) the UK, (c) Norway.

a) Results derived from 10 % VOC emission reduction scenarios

Emitter Country						
		HU	NO	PL	ES	UK
R e c e i v e r C o u n t r y	Albania	25.46	0.00	26.04	0.00	0.00
	Austria	174.89	15.85	231.13	16.94	218.89
	Belgium	131.29	40.96	812.16	16.97	1231.11
	Bulgaria	24.55	0.35	96.89	0.00	0.00
	Czech.	468.76	9.06	988.62	17.45	229.60
	Denmark	16.41	1.41	330.20	0.03	317.02
	Finland	1.17	0.01	12.89	0.00	23.27
	France	77.34	33.74	317.87	25.36	747.68
	GDR	188.96	24.39	708.40	16.37	257.18
	FRG	293.26	53.79	502.60	26.31	537.23
	Greece	14.55	0.05	36.76	0.68	0.00
	Hungary	602.24	0.66	861.16	1.75	57.97
	Ireland	3.46	6.02	152.24	0.12	845.83
	Italy	108.53	9.98	120.34	14.40	135.64
	Lux.	252.34	76.43	1089.31	35.07	1575.64
	Netherl.	104.95	14.04	317.94	9.90	685.24
	Norway	0.40	1.27	20.99	0.00	23.88
	Poland	332.36	3.00	873.10	3.13	104.97
	Portugal	0.00	0.00	0.00	156.80	0.04
	Romania	175.08	0.09	235.95	0.00	6.05
	Spain	0.00	0.98	7.23	105.12	36.00
	Sweden	22.49	0.91	153.39	0.05	53.08
	Switz.	305.28	47.86	97.53	20.90	646.11
	Turkey	0.21	0.00	7.75	0.09	0.00
	USSR	28.52	0.17	51.54	0.00	6.34
	UK	6.47	28.41	209.69	2.76	989.93
	Yugosl.	119.43	3.69	177.79	5.02	15.95
Mean		45.16	4.08	70.05	7.98	29.50

Table 8(a). Decreases in excess ozone (April-Sept. 1989) in 27 European countries per unit VOC emission reduced from 5 emitter countries: Hungary (HU), Norway (NO), Poland (PL), Spain (ES), and the UK. Derived from results of 10% VOC emission reduction scenarios (see note below). The "mean" change is the average over all European land areas. Units: ppt.hours per grid square per ktonne VOC reduced.

NB. All changes in excess ozone are scaled by the amount of VOC emission reduction in each country, to give changes in ppt.hours per grid square per ktonne VOC. For example, Hungary has an annual VOC emission of 205 ktonnes. A 10 % reduction in Hungary's VOC emissions leads to a reduction in excess ozone concentrations over Austria of 3585 ppt.hours (per grid square). Therefore the change in excess ozone per unit VOC emission reduced in Hungary is $3583 \text{ ppt.hours} / (10 \% \times 205 \text{ ktonnes}) = 174.89 \text{ ppt.hours per grid square per ktonne}$.

b) Results derived from 30 % VOC emission reduction scenarios

Emitter Country						
		HU	NO	PL	ES	UK
R e c e i v e r C o u n t r y	Albania	24.80	0.00	22.27	0.00	0.00
	Austria	168.80	14.66	206.27	17.04	204.65
	Belgium	128.05	38.81	801.92	16.40	1055.89
	Bulgaria	24.46	0.34	98.06	0.00	0.00
	Czech.	455.28	8.24	952.54	17.53	217.33
	Denmark	14.23	1.22	334.00	0.03	225.38
	Finland	1.15	0.01	12.82	0.00	15.52
	France	75.76	31.75	311.70	25.23	659.70
	GDR	184.77	22.71	699.31	16.23	260.63
	FRG	285.02	51.08	485.46	26.73	519.86
	Greece	14.12	0.05	33.94	0.69	0.00
	Hungary	579.20	0.59	836.35	1.79	59.38
	Ireland	3.33	5.38	151.05	0.11	680.18
	Italy	104.57	9.62	120.16	14.58	123.39
	Lux.	243.89	73.10	1040.44	30.80	1120.87
	Netherl.	103.70	13.05	313.54	10.73	639.35
	Norway	0.39	1.18	20.97	0.00	23.46
	Poland	322.60	2.77	855.80	3.13	99.08
	Portugal	0.00	0.00	0.00	153.90	0.04
	Romania	169.52	0.07	228.07	0.00	5.90
	Spain	0.00	0.88	7.14	108.41	30.65
	Sweden	21.12	0.84	151.76	0.05	51.19
	Switz.	299.51	45.93	96.95	21.13	582.28
	Turkey	0.20	0.00	7.55	0.10	0.00
	USSR	27.32	0.16	50.06	0.00	5.62
	UK	6.31	26.60	211.12	2.75	903.37
	Yugosl.	114.10	3.59	175.18	5.04	13.21
	Mean	43.69	3.85	22.97	8.11	20.04

Table 8(b). Decreases in excess ozone (April-Sept. 1989) in 27 European countries per unit VOC emission reduced from 5 emitter countries. Derived from results of 30% VOC emission reduction scenarios (see notes in Table 7(a)).

c) Results derived from 50 % VOC emission reduction scenarios

Emitter Country						
		HU	NO	PL	ES	UK
R e c e i v e r C o u n t r y	Albania	24.90	0.00	20.47	0.00	0.00
	Austria	166.65	13.69	185.69	17.14	178.57
	Belgium	127.47	37.68	796.96	15.92	899.27
	Bulgaria	24.77	0.33	96.64	0.00	0.00
	Czech.	451.59	7.87	920.73	17.78	210.72
	Denmark	12.59	1.16	333.52	0.03	195.56
	Finland	1.15	0.01	13.06	0.00	12.76
	France	75.48	30.81	311.09	24.82	566.03
	GDR	185.27	21.78	690.82	16.40	251.75
	FRG	283.92	49.97	477.46	27.03	513.30
	Greece	13.81	0.04	32.33	0.70	0.00
	Hungary	567.53	0.57	801.20	1.80	58.93
	Ireland	3.32	5.11	151.09	0.11	622.00
	Italy	101.91	9.27	120.78	14.68	105.01
	Lux.	242.16	71.34	1056.84	25.88	960.22
	Netherl.	104.35	12.77	307.62	10.92	597.15
	Norway	0.39	1.13	19.71	0.00	22.79
	Poland	315.73	2.66	837.22	3.17	94.71
	Portugal	0.00	0.00	0.00	151.49	0.04
	Romania	165.22	0.06	219.88	0.00	5.55
	Spain	0.00	0.84	7.18	111.94	24.46
	Sweden	20.30	0.80	141.22	0.05	41.97
	Switz.	298.41	45.18	98.37	21.40	540.36
	Turkey	0.20	0.00	6.89	0.10	0.00
	USSR	26.88	0.16	48.21	0.00	4.88
	UK	6.26	25.88	214.48	2.82	830.91
	Yugosl.	111.05	3.09	172.02	5.06	10.72
Total		43.03	3.72	8.46	3.64	6.72

Table 8(c). Decreases in excess ozone (April-Sept. 1989) in 27 European countries per unit VOC emission reduced from 5 emitter countries. Derived from results of 50% VOC emission reduction scenarios (see notes in Table 8(a)).

3.5.2 The effect of low NO_x emission levels

The base-run described in section 3.4 above, and the 30% VOC reduction scenarios have been re-run, but this time with all runs being conducted with NO_x emissions being set to half of the 1989 levels. The aim of this experiment is to see how great an effect this new NO_x level has on the "blame-matrices" calculated for VOC reductions.

The re-calculated effects of the 30% VOC emission scenarios on mean and excess ozone are shown in Tables 9(a),(b). It is immediately clear that the new NO_x levels do indeed change the blame-matrices in a significant way. However, there are some clear patterns in the changes, with the effect of VOC emissions reductions at half of 1989 NO_x levels being approximately half of that found for the 1989 levels in many cases. The ratio of the ozone reductions obtained in each grid square in the 1989 NO_x level case to that obtained in the new low NO_x level case is illustrated in Figure 10. Time has not yet allowed a thorough investigation of these results, but in many ways the results obtained in Table 9 and Figure 10 follow the behaviour expected in different NO_x regimes. For example, production of ozone in areas of high NO_x concentration should be sensitive to VOCs, but relatively insensitive to NO_x, thus the effectiveness of VOCs should also be relatively insensitive to the NO_x emissions level (cf. the contribution of the UK to itself). Ozone production in low NO_x areas should be approximately proportional to NO_x (eg. Sillman et al. 1990), which explains the factor of 2 reduction in the effectiveness of VOCs seen in many areas, and in most relationships in the blame matrix. Detailed analysis is complicated because of the long time-periods under consideration (and hence the wide combination of meteorological and chemical conditions), and the fact that along a 96 h trajectory many different production regimes can be experienced.

In summary, it would seem that although the NO_x emission level does change the blame-matrix obtained for the effects of 30% VOC control, the main change is in the absolute effectiveness of VOC control (ie. in the amount of O₃ reduction obtained) rather than in the assessment of the relative effectiveness of VOC between different countries.

3.6 Discussion

The linearities found above for the response of mean ozone concentrations to VOC emission reductions suggest that we can construct a blame-matrix for ozone which is reasonably robust against moderate VOC changes in the vicinity of the source areas. Such a blame-matrix will be presented in section 3.7. This blame-matrix should be considered with its limitations however.

As shown in section 3.5.2, substantial changes in NO_x emissions will change the pattern of ozone production, so the blame-matrix should only be taken as a guide as to the effect of VOC reductions at NO_x levels not too different from those of 1989. Also, the linearities found arise from the fact that, in general, changing one country's VOC emissions has little effect on OH and HO₂/RO₂ concentrations along a trajectory. If the general level of VOC changes, we might expect OH and HO₂/RO₂ to also change, introducing a non-linearity we have not yet quantified.

Further, there are great uncertainties surrounding the magnitude and importance of natural

Results derived from 30 % VOC emission reduction scenarios: low NO_x levels

Emitter Country						
		HU	NO	PL	ES	UK
R e c e i v e r C o u n t r y	Albania	0.10	0.00	0.05	0.00	0.00
	Austria	0.16	0.03	0.14	0.01	0.09
	Belgium	0.03	0.07	0.18	0.02	1.01
	Bulgaria	0.11	0.01	0.07	0.00	0.00
	Czech.	0.33	0.02	0.42	0.01	0.10
	Denmark	0.03	0.04	0.11	0.01	0.25
	Finland	0.01	0.02	0.03	0.00	0.06
	France	0.02	0.04	0.07	0.07	0.48
	GDR	0.10	0.05	0.27	0.02	0.25
	FRG	0.06	0.06	0.15	0.03	0.39
	Greece	0.08	0.00	0.04	0.00	0.00
	Hungary	0.66	0.02	0.34	0.00	0.03
	Ireland	0.00	0.00	0.03	0.00	0.30
	Italy	0.11	0.01	0.06	0.03	0.07
	Lux.	0.04	0.09	0.17	0.03	0.57
	Netherl.	0.03	0.03	0.15	0.02	0.90
	Norway	0.01	0.04	0.02	0.00	0.07
	Poland	0.19	0.03	0.41	0.00	0.10
	Portugal	0.00	0.00	0.00	0.60	0.04
	Romania	0.25	0.01	0.15	0.00	0.01
	Spain	0.00	0.01	0.00	0.38	0.10
	Sweden	0.03	0.05	0.07	0.00	0.08
	Switz.	0.05	0.02	0.03	0.04	0.22
	Turkey	0.03	0.00	0.02	0.00	0.00
	USSR	0.03	0.01	0.05	0.00	0.02
	UK	0.01	0.03	0.05	0.00	1.22
	Yugosl.	0.24	0.01	0.12	0.00	0.01
	Mean	0.04	0.01	0.05	0.02	0.08

Table 9(a). Decreases in mean ozone in 27 European countries per unit VOC emission reduced from 5 emitter countries when NO_x emissions levels are set at half of 1989 values in base and scenario runs. Derived from results of 30% VOC emission reduction scenarios (see note in Table 7(a)). Units: ppt per ktonne VOC reduced.

Results derived from 30 % VOC emission reduction scenarios: low NO_x levels

Emitter Country						
		HU	NO	PL	ES	UK
R e c e i v e r C o u n t r y	Albania	4.12	0.00	0.57	0.00	0.00
	Austria	21.82	0.79	39.60	3.63	100.73
	Belgium	62.04	41.14	502.91	1.91	1090.05
	Bulgaria	-0.04	0.00	1.46	0.00	0.00
	Czech.	73.48	0.33	244.22	8.44	98.11
	Denmark	16.17	0.11	157.67	0.02	169.35
	Finland	0.12	0.01	3.17	0.00	7.50
	France	25.80	17.36	146.07	5.00	425.79
	GDR	96.65	4.83	212.03	8.96	148.82
	FRG	95.13	17.46	174.67	8.54	415.08
	Greece	1.32	0.00	3.71	0.00	0.00
	Hungary	51.36	0.00	167.60	0.04	33.99
	Ireland	2.45	2.92	98.80	0.04	346.72
	Italy	6.30	1.54	21.53	0.08	68.27
	Lux.	161.18	118.15	469.38	2.25	801.28
	Netherl.	55.54	7.85	241.78	4.63	738.53
	Norway	1.58	0.45	5.61	0.00	11.22
	Poland	59.57	0.42	175.09	1.01	37.19
	Portugal	0.00	0.00	0.00	57.20	-0.00
	Romania	7.68	0.00	30.60	0.00	1.65
	Spain	0.00	0.03	1.45	18.06	7.30
	Sweden	9.70	0.16	56.19	0.00	17.85
	Switz.	35.66	0.87	9.40	0.00	351.87
	Turkey	0.01	0.00	0.30	0.00	0.00
	USSR	1.00	0.00	6.67	0.00	2.50
	UK	7.78	12.80	138.93	1.13	1229.22
	Yugosl.	3.55	0.04	30.71	1.74	5.29
Mean		7.58	1.51	22.73	1.74	15.26

Table 9(b). Decreases in excess ozone (April-Sept. 1989) in 27 European countries per unit VOC emission reduced from 5 emitter countries when NO_x emissions levels are set at half of 1989 values in base and scenario runs. Derived from results of 30% VOC emission reduction scenarios (see note in Table 8(a)). Units: ppt.hours per grid square per ktonne VOC reduced.

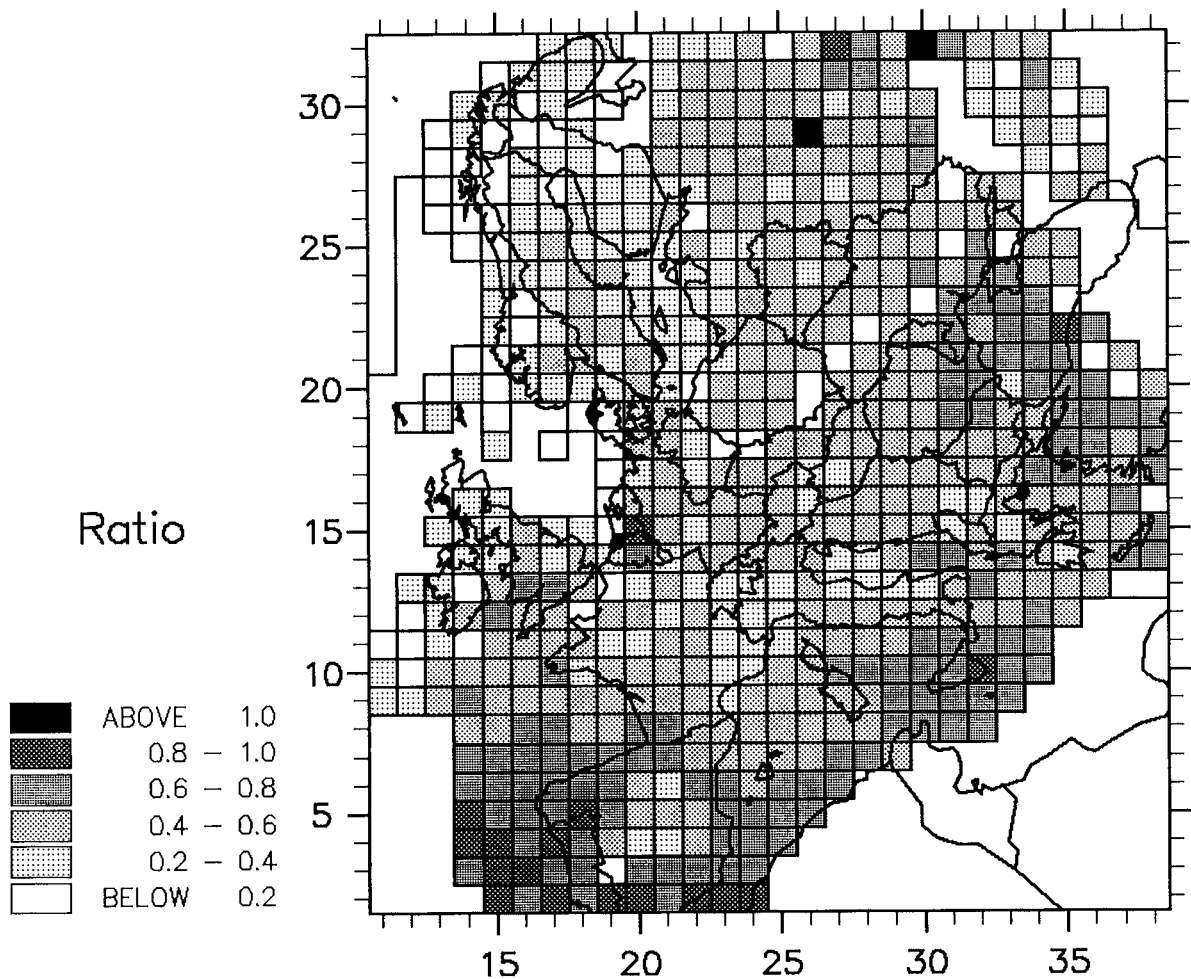


Figure 10. Ratio of ΔO_3 {1989 NO_x emissions, 30% VOC control} : ΔO_3 {0.5 x 1989 NO_x emissions, 30% VOC control}, where ΔO_3 {case, 30% VOC control} refers to the reductions in mean ozone caused by 30% VOC control in the case of either 1989 NO_x emission levels (section 3.5.1) or 0.5 x 1989 NO_x emission levels (section 3.5.2).

VOC which we have not addressed in this study. At present natural VOCs are predicted to be of great importance in Mediterranean countries. If these natural VOCs are significantly different to those estimated here, this might result in a substantial change in the relative contribution of anthropogenic VOC from countries such as Spain to ozone formation.

It is also important to be clear about the meaning of "linearity" in the above experiments. We have shown that a 5x % reduction in VOC emissions from one country alone leads to 5 times the reduction in mean ozone that an x % VOC reduction in VOC from that country produces. We have not shown that results from different countries can be superimposed in a linear way. In other words, if VOC reduction in country i leads to a change in ozone ΔO_3^i , and VOC reduction in country j leads to a change in ozone ΔO_3^j , then we have not demonstrated that the change in ozone when both countries reduce VOC emissions simultaneously, ΔO_3^{i+j} , is equal to the sum of $\Delta O_3^i + \Delta O_3^j$.

To anticipate the results of section 3.7 a little, for June 1989 we have in fact compared the ozone changes produced by reducing the VOC emissions of all European countries by 30% with the sum of the ozone reductions obtained by reducing the VOC emissions of each country separately. The results, illustrated as a scatter plot of individual grid values in Figure 11, are as expected somewhat different in the two cases. The "real" calculation of 30% VOC emission reductions gives a somewhat smaller decrease in ozone concentrations than the sum of the county-to-country contributions. This can be explained by the general lowering of photochemical activity (lower OH, HO₂, and RO₂ concentrations) in the "real" 30 % run compared to the country specific runs.

However, the correlation between the two sets of results is very good ($r=0.92$), and the differences in the magnitude of the ozone differences is not so great considering the simplifications inherent in summing contributions from the country-to-country model. Given that we are most interested in comparing the relative contributions of one country with another, this comparison suggests that the calculation of country-to-country contributions individually is unlikely to lead to large errors.

Thus, despite the qualifications given above, it is still very likely that the country-to-country comparisons presented in sections 3.5 above do give a good representation of the differences in the ozone producing capacities of VOCs from different countries, at least in present day conditions.

3.7 A blame-matrix for ozone.

The blame-matrix giving the absolute changes in mean ozone resulting from 30% reductions in VOC from all countries is presented in Table 10. The equivalent blame matrix in terms of ozone changes per unit VOC reduction is given in Table 11. If we consider first the absolute changes, the countries whose VOC emission contributes most to ozone formation in Europe are predicted to be France, F.R.G, the U.K, and the Soviet Union. Of course, these relative contributions are strongly influenced by the different emission levels between countries. When we consider the ozone changes per unit VOC emission (Table 11), the country contributions

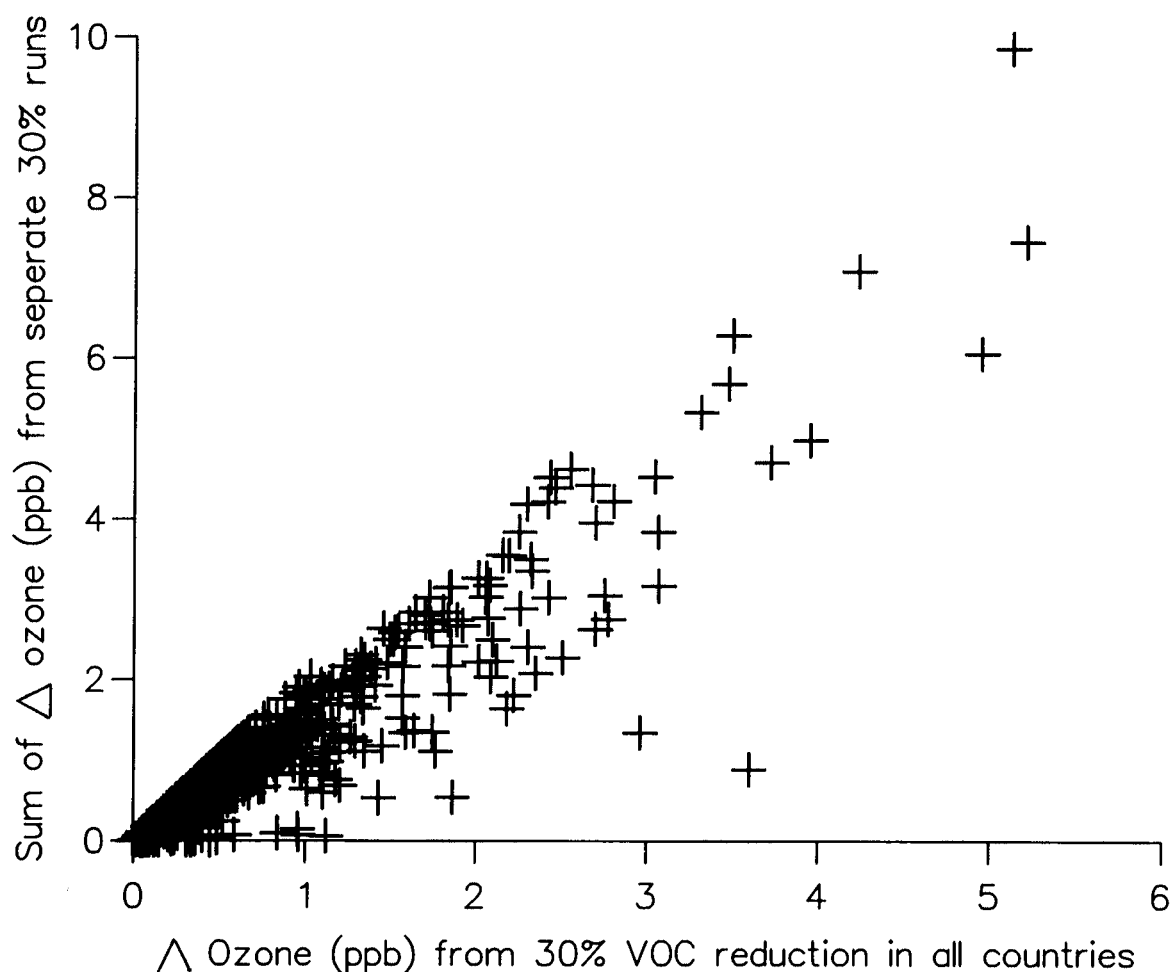


Figure 11. Comparison for each grid square of the sum of the ozone reductions (in ppb) obtained from reducing VOC emissions in each of 27 countries by 30 % separately against the ozone reduction obtained by a 30% reduction in all countries simultaneously. June 1989.

are much more evenly distributed. A group of countries, lying roughly in N.W. Europe, contribute over 0.1 ppt O_3 per grid square per ktonne VOC, with the Netherlands and Belgium contributing most. Countries in other areas, including Scandinavia, most of the Mediterranean countries, and the Soviet Union, contribute considerably less to ozone formation in Europe, typically 0.02-0.06 ppt O_3 per grid square per ktonne VOC.

These different contributions can be well explained by the factors discussed for our 5 example countries in section 3.5.1.

Table 10 (a). A Blame Matrix for Ozone: per 30 % reduction in VOC Emissions

The figures give the reductions in 6-monthly mean ozone (in ppt) in each receiver country arising from a 30% reduction in VOC emissions from each emitter country. All NO_x emissions are held at 1989 levels. The "mean" is the average ozone reduction over all European land areas.

		Emitter Country														
		AL	AT	BE	BG	CS	DK	FI	FR	DD	DE	GR	HU	IE	IT	
R e c e i v e r C o u n t r y	AL	9	14	4	6	14	3	1	21	27	33	40	12	0	109	
	AT	0	76	53	1	44	18	4	165	167	483	1	23	2	341	
	BE	0	35	257	0	29	21	2	482	205	810	0	3	11	19	
	BG	3	13	2	14	14	4	2	6	23	31	34	16	0	26	
	CS	0	66	43	1	87	23	7	135	255	519	2	39	2	93	
	DK	0	10	38	0	15	52	4	93	93	228	0	4	8	13	
	FI	0	2	6	0	3	12	12	20	17	35	0	1	1	1	
	FR	0	14	132	0	14	14	1	526	140	530	0	2	7	54	
	DD	0	34	84	0	39	38	7	254	374	777	1	13	8	57	
	DE	0	37	142	0	30	29	4	350	268	1061	1	8	8	111	
	GR	10	9	2	10	7	2	1	17	16	19	126	8	0	55	
	HU	0	60	17	4	64	13	4	46	88	184	5	78	1	122	
	IE	0	1	13	0	3	5	0	34	26	66	0	0	28	0	
	IT	1	23	31	2	15	8	1	179	64	163	4	12	1	483	
	LU	0	64	293	0	35	37	2	597	213	1136	0	5	7	52	
	NL	0	14	158	0	20	20	2	304	168	644	0	3	14	10	
	NO	0	3	7	0	4	6	3	22	19	38	0	1	2	5	
	PL	0	39	24	2	43	31	7	96	192	329	2	24	3	41	
	PT	0	0	5	0	0	0	0	86	4	31	0	0	2	1	
	RO	1	20	5	8	27	5	2	11	42	65	11	33	0	42	
	ES	0	0	27	0	1	1	0	155	14	84	0	0	2	7	
	SE	0	8	11	0	11	20	5	36	41	74	0	5	3	13	
	CH	0	27	133	0	11	22	2	385	232	786	0	7	3	367	
	TR	1	2	1	2	2	0	0	2	3	4	22	3	0	5	
	SU	0	3	3	1	5	6	5	8	19	34	1	4	0	4	
	GB	0	2	35	0	5	10	1	106	47	183	0	1	21	1	
	YU	2	32	6	7	27	7	3	32	52	80	14	30	0	164	
Mean		0	7	16	1	8	6	2	57	36	97	4	5	2	30	

Table 10 (b). A Blame Matrix for Ozone: per 30 % reduction in VOC Emissions

The figures give the reductions in 6-monthly mean ozone (in ppt) in each receiver country arising from a 30% reduction in VOC emissions from each emitter country. All NO_x emissions are held at 1989 levels. The "mean" is the average ozone reduction over all European land areas.

		Emitter Country												
		LU	NL	NO	PL	PT	RO	ES	SE	CH	TR	SU	GB	YU
Receiver Country	AL	0	5	1	32	0	7	1	2	2	1	35	6	21
	AT	2	90	5	108	0	18	4	20	45	0	62	148	21
	BE	5	301	9	118	0	1	11	21	14	0	26	928	1
	BG	0	3	1	56	0	22	0	4	1	8	107	2	14
	CS	2	91	4	292	0	20	3	22	15	0	141	132	20
	DK	1	66	8	62	0	2	5	35	3	0	27	327	3
	FI	0	10	4	23	0	1	0	28	0	0	68	58	0
	FR	4	144	6	44	1	1	31	10	18	0	12	600	2
	DD	3	136	8	169	0	5	7	27	13	0	65	305	6
	DE	5	232	8	107	0	3	10	23	37	0	45	456	5
	GR	0	2	0	22	0	10	2	2	2	9	82	2	11
	HU	1	32	3	244	0	40	2	12	5	1	139	45	39
	IE	0	19	1	13	0	0	1	5	0	0	3	330	0
	IT	1	38	2	39	0	7	12	9	24	0	15	90	22
	LU	13	343	14	123	0	0	14	24	41	0	34	716	1
	NL	2	284	4	101	0	0	10	21	7	0	28	805	1
	NO	0	10	9	13	0	1	1	12	1	0	15	74	1
	PL	1	54	5	273	0	14	1	31	8	1	147	124	17
	PT	0	7	0	0	280	0	259	0	1	0	0	37	0
	RO	0	10	1	104	0	46	1	8	1	4	148	7	23
	ES	1	23	1	2	66	0	182	1	1	0	0	84	0
	SE	0	20	9	51	0	2	1	38	2	0	29	98	2
	CH	5	167	4	24	0	3	20	16	139	0	16	357	10
	TR	0	1	0	9	0	6	0	0	0	27	152	0	2
	SU	0	7	1	32	0	6	0	11	0	1	299	20	2
	GB	1	66	4	28	0	0	2	8	1	0	14	858	0
	YU	0	11	2	80	0	22	2	7	5	1	55	16	39
Mean		1	23	2	33	5	5	11	8	4	2	97	80	4

Table 11 (a). A Blame Matrix for Ozone: per unit VOC emissions reduction

The figures give the reductions in 6-monthly mean ozone (in 0.01 ppt) in each receiver country estimated to occur for each unit (1 ktonne) reduction in each emitter country's national VOC emissions. These ppt per ktonne changes are determined derived from the 30% VOC reduction results given in Table 10, compensating for the magnitude of the emissions change in each country as explained in Table 7(a). All NO_x emissions are held at 1989 levels.

		Emitter Country														
		AL	AT	BE	BG	CS	DK	FI	FR	DD	DE	GR	HU	IE	IT	
R e c e i v e r C o u n t r y	AL	90	11	4	12	16	5	2	3	9	4	73	19	0	22	
	AT	2	62	53	2	50	35	8	28	53	63	1	37	7	69	
	BE	0	29	256	0	33	39	4	82	65	106	0	5	42	4	
	BG	29	11	2	27	16	8	4	1	7	4	61	26	0	5	
	CS	5	54	43	3	99	44	14	23	81	68	4	63	9	19	
	DK	2	8	38	1	17	98	8	16	30	30	1	6	31	3	
	FI	0	1	6	0	3	22	25	3	5	5	0	2	5	0	
	FR	1	11	131	0	16	27	2	89	44	70	0	4	26	11	
	DD	2	28	83	1	44	73	14	43	119	102	1	20	28	12	
	DE	2	30	141	1	34	56	8	59	85	140	2	14	29	23	
	GR	100	8	2	20	8	3	1	3	5	2	227	14	0	11	
	HU	4	49	17	7	73	25	9	8	28	24	8	127	3	25	
	IE	0	1	13	0	4	10	1	6	8	9	0	0	103	0	
	IT	12	19	31	4	16	15	2	30	20	21	6	20	3	98	
	LU	0	52	291	0	40	69	4	101	67	149	0	7	25	11	
	NL	0	11	157	0	22	39	5	51	53	85	0	5	52	2	
	NO	0	2	7	1	5	12	7	4	6	5	0	2	7	1	
	PL	5	32	24	3	48	58	14	16	61	43	3	39	12	8	
	PT	0	0	5	0	0	1	0	15	1	4	0	0	6	0	
	RO	8	16	5	15	31	9	5	2	13	8	20	54	1	8	
	ES	0	0	27	0	1	2	0	26	4	11	1	0	8	2	
	SE	0	6	11	1	13	37	9	6	13	10	0	9	10	3	
	CH	2	22	132	0	12	43	4	65	74	103	1	12	10	74	
	TR	9	2	1	4	3	0	1	0	1	1	40	5	0	1	
	SU	1	3	3	2	6	12	9	1	6	4	2	6	2	1	
	GB	0	2	34	0	6	19	2	18	15	24	0	1	78	0	
	YU	20	26	6	14	30	14	6	5	17	10	25	49	0	33	
Mean	3	6	16	2	9	12	5	10	11	13	7	8	6	6		

Table 11 (b). A Blame Matrix for Ozone: per unit VOC emissions reduction

The figures give the reductions in 6-monthly mean ozone (in 0.01 ppt) in each receiver country estimated to occur for each unit (1 ktonne) reduction in each emitter country's national VOC emissions. These ppt per ktonne changes are determined derived from the 30% VOC reduction results given in Table 10, compensating for the magnitude of the emissions change in each country as explained in Table 7(a). All NO_x emissions are held at 1989 levels.

	Emitter Country												
	LU	NL	NO	PL	PT	RO	ES	SE	CH	TR	SU	GB	YU
R e c e i v e r C o u n t r y	AL	3	4	1	10	0	6	1	2	2	1	1	25
	AT	53	68	7	32	0	15	2	15	51	0	2	24
	BE	128	227	13	35	0	1	4	15	16	0	1	1
	BG	1	3	1	16	0	19	0	3	1	10	4	16
	CS	56	68	6	86	0	17	1	16	17	0	5	23
	DK	21	50	13	18	0	2	2	25	3	0	1	3
	FI	4	8	6	7	0	1	0	21	0	0	2	1
	FR	96	109	10	13	2	1	12	7	20	0	0	3
	DD	80	103	12	50	1	5	3	20	15	0	2	7
	DE	134	175	13	32	0	3	4	16	41	0	2	5
	GR	2	2	1	7	0	9	1	1	2	12	3	13
	HU	17	24	4	72	0	35	1	9	6	1	5	45
	IE	5	14	2	4	0	0	0	3	0	0	0	0
	IT	33	28	4	12	1	6	5	6	27	0	1	26
	LU	325	258	22	36	0	0	5	18	46	0	1	1
	NL	63	214	7	30	0	0	4	15	8	0	1	1
	NO	5	8	14	4	0	1	0	8	1	0	1	1
	PL	30	41	8	80	0	12	1	22	9	1	5	19
	PT	8	5	0	0	626	0	96	0	1	0	0	0
	RO	3	7	2	31	0	40	0	6	1	5	5	26
	ES	19	18	1	1	148	0	67	0	1	0	0	0
	SE	7	15	14	15	0	2	0	27	2	0	1	2
	CH	127	126	6	7	0	3	7	12	156	0	1	12
	TR	0	1	0	3	0	5	0	0	0	34	6	3
	SU	2	5	2	9	0	5	0	8	0	1	11	2
	GB	21	50	5	8	0	0	1	6	1	0	1	0
	YU	5	9	3	24	0	19	1	5	6	1	2	45
Mean	13	17	3	10	10	4	4	6	4	2	4	13	4

8. SUMMARY AND CONCLUSIONS

The EMEP MSC-W ozone model has been used in two studies to evaluate the effectiveness of particular anthropogenic VOC emission reductions in reducing mean and elevated ozone concentrations:

(A) Hydrocarbon reactivity and ozone formation in Europe.

We have shown that many of the variations in ozone forming potentials of different VOC species can be explained in terms of the time-scales for reaction of the initial VOC species, and of its degradation products. These time-scales have been quantified using the EMEP MSC-W ozone model, and used to show why the POCP of a species such as n-butane can be expected to increase significantly during photochemical episodes, and over multi-day transport events. These time-scale considerations also suggest that variations in POCP values between months should be large. An example calculation using n-butane strikingly confirms this monthly difference.

(B) On the linearity of country-to-country ozone calculations in Europe.

A comparison of the effects of making equivalent VOC emission reductions in five different countries was conducted to investigate the linearity of ozone changes in Europe to VOC emission changes. The results showed a very strong linearity in the results for mean ozone (in the sense that a 5x % reduction in VOC emissions from a country leads to 5 times the reduction in mean ozone that an x % reduction produces).

As expected, calculations also show that the blame matrix obtained is a function of the NO_x emission level used in the calculations. However, in most cases it is the absolute effectiveness of VOC emissions reduction that changes (measured in ppt ozone per ktonne VOC reduced), rather than the relative contribution between different countries.

Given the linearities found in the system, and recognising the limits of application with respect to simultaneous VOC & NO_x control, it seems as if a blame-matrix for ozone does give useful information on the relative contribution of VOC emissions from different countries to ozone formation in Europe. Such a blame-matrix has been presented for the summer of 1989.

9. References

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