

Development of a reactivity index for the control of the emissions of organic compounds

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Statement of Use

This research represents the initial stage in the development of a risk-based approach to the regulation of VOC compounds according to their propensity to produce ozone. It will provide agreed approaches and guidance for operational PIR staff in the authorisation of IPC/IPPC processes and support for PIR policy purposes.

Keywords

Photochemical ozone creation, volatile organic compounds, industrial emissions, reactivity

Research Contractor

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EXECUTIVE SUMMARY

This study investigates whether current understanding of photochemical ozone formation is advanced and detailed enough to design control strategies for organic compound emissions, which differentiate between the different species. A relationship is constructed between the emissions of close on 100 individual volatile organic compounds (VOCs) and downwind ozone produced by them. Such a relationship should exist from a theoretical standpoint. We investigate here whether it is robust enough to be of practical use in the design of pollution control strategies for organic compounds in the UK. For the relationship to be useful it must be consistent under a range of realistic atmospheric conditions and this study reports on ozone produced for a carefully chosen, but limited number of situations.

The research is based on a very detailed chemical mechanism involving 120 VOC species following the development of chemistry within an air parcel crossing the country. The main conclusion from the work is that for each individual VOC, one could derive an estimate of the ozone production in ppb per tonne/hour of emitted VOC. This could also be expressed as an emission ceiling for each emitted VOC in tonne/hour. This was felt to be preferable to a method based on the concept of a photochemical oxidising potential.

For the method to have practical regulatory use, the environmental impact associated with each VOC must be associated with a single quantity. In this study, following the sensitivity experiments conducted, the maximum integrated downwind ozone production (maximum IDOP) in ppb per VOC emission rate in tonne hr⁻¹ was chosen as the indicator. This represents a precautionary approach. The maximum IDOP for most VOCs largely occurs under the same assumed emissions condition. The question arises whether the assumptions for this condition represent a representative regulatory situation. Although the method shows promise, before applying the method routinely, it requires further assessments and checks to see whether its range of application corresponds closely to actual release conditions at plants in England and Wales. It should also be made compatible with the Agency's Pollution Inventory in as far as both the Inventory and the ozone assessment methods should use the same VOC classification.

A practical application of the method is shown in a worked example involving metal surface cleaning, using either organic or halocarbon solvents. This example raises the further question as to whether sectors should be given the mass emission reduction targets based on typical VOC characteristics, or whether a strategy should focus on individual species. These strategies can then be compared with the flat-rate, across-the-board national emission reduction strategies for VOCs, within the UN ECE Gothenburg Protocol and the EU National Emission Ceilings Directive.

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1. INTRODUCTION

The mechanism of photochemical ozone formation has been developed from a combination of smog chamber experiments, laboratory chemistry studies and field observations. This theoretical framework provides the underpinning for current policy approaches to the reduction of ozone exposures, through the control of ozone precursor emissions.

At its most simplest level, understanding of the mechanism of photochemical ozone formation points to organic compounds and oxides of nitrogen as being the sole ozone precursors. Emissions of organic compounds and nitrogen oxides are therefore the prime targets for ozone reduction policies. These targets are generally set as percentage reductions across the entire inventory for each member state (UN ECE 1991). This is the way that the control of nitrogen oxides and volatile organic compounds has been implemented through the European Community National Emissions Ceilings Directive and the UN ECE Gothenburg Protocol.

At the next level of complexity, the theoretical underpinning suggests that each organic compound makes a different contribution to ozone formation, and control strategies for organic compound emissions should take these differences into account. They should focus on those compounds which contribute most to ozone formation and least on those that do not contribute significantly. Since the different emission sources of organic compounds are likely to emit a different mix of organic compounds, control strategies should focus their efforts on those sources or installations that contribute most to ozone formation.

This is the focus of the present study, which asks the question whether current understanding of photochemical ozone formation is advanced and detailed enough to design control strategies for organic compound emissions, which differentiate between the different species. A detailed Master Chemical Mechanism is used to describe ozone formation downwind of a hypothetical industrial installation in the British Isles that is emitting organic compounds. A relationship is constructed between the emissions of close on 100 individual organic compounds and downwind ozone produced by them. Such a relationship should exist from a theoretical standpoint. We investigate here whether it is robust enough to be of practical use in the design of pollution control strategies for organic compounds in the UK. For the relationship to be useful it must be consistent under a range of realistic atmospheric conditions and this study reports on ozone produced for a carefully chosen, but limited, number of situations.

2. THE UK PHOTOCHEMICAL TRAJECTORY MODEL

2.1 Model Description

In previous studies, a photochemical trajectory model has been employed to describe regional scale ozone, PAN and hydrogen peroxide formation over Europe (Hough and Derwent 1987; Derwent and Davies, 1994). A box-model is used to describe the chemical development of ozone in a single air parcel with its base on the ground, its upper lid at the top of the boundary layer and with horizontal dimensions 10 km x 10 km. In the base case model experiment, the highly idealised anticyclonic meteorological situation of easterly winds, leading to a broad air flow carrying photochemically-aged

polluted air masses out of Europe towards the British Isles, was adopted, as described in previous studies. This experiment addresses conditions considered typical of multi-day ozone episodes over north-west Europe and not necessarily those that would maximise local ozone formation over the United Kingdom.

The details of the emission inventories employed, including the speciation of the organic compounds, are as given in a previous study (Derwent et al. 1998). A single-layer trajectory model is used and the nighttime chemistry of any material trapped above the nocturnal boundary layer has been neglected. Previous work (Hough and Derwent 1987) has shown that this simplification does not lead to appreciable errors when studying the small differences in ozone formation caused by the different hydrocarbons. The sensitivity and uncertainty in the photochemical trajectory model ozone responses to changes in precursor emissions, due to meteorological and other variables have been described elsewhere (Hov and Derwent 1988).

2.2 Master Chemical Mechanism (MCM)

The fundamental principle underlying the Master Chemical Mechanism (MCM) is that the chemistry believed to account for the degradation of organic compounds, and the associated production of ozone and other secondary pollutants, can be built up reliably from the known chemistry of the small number of hydrocarbon oxidation systems which have been studied in detail in laboratory and smog chamber systems. The MCM version 1.0 employed in the photochemical trajectory model describes the oxidation of methane, 95 organic compounds in the UK speciated organic compound inventory (UK PORG 1997), 24 additional organic compounds, carbon monoxide, sulphur dioxide and NO_x (Saunders et al., 1997). It was constructed mainly using evaluated chemical kinetic databases for the simple reactions of the O, H, and N atoms and free radicals (Atkinson et al. 1996; DeMore et al. 1994) and a protocol defined on the basis of available laboratory measurements of the kinetics and products of elementary reactions involved in the degradation of organic compounds (Jenkin et al., 1997). It is designed to describe the chemistry under a wide range of ambient conditions appropriate to the boundary layer and is therefore suitable for comparative assessments of the formation of secondary pollutants, such as ozone and PAN, from the tropospheric oxidation of organic compounds.

The MCMv1.0 comprises over 2400 chemical species and over 7100 chemical reactions, and may be viewed and downloaded via the world wide web at: (<http://chem.leeds.ac.uk:80/Atmospheric/MCM/mcmproj.html>).

The photochemical model, utilising a previous version of the chemical mechanism, was a full participant in the IPCC Photocomp model intercomparison (Olsen et al. 1997). This intercomparison involved a study of the photolysis rates and calculated concentrations for a range of scenario cases relevant to regional and global ozone formation. The results obtained with the UK photochemical trajectory model were well within the uncertainty bounds of the group of models tested, for all the concentration outcomes.

2.3 Base Case Model Experiment

The system of over 2400 simultaneous stiff differential equations was integrated with a variable order Gear's method using the computer code FACSIMILE (Curtis and Sweetenham, 1987). For a small number of species, initial concentrations were set at central European levels for a polluted boundary layer situation, as follows: NO 2 ppb, NO₂ 6 ppb, SO₂ 5 ppb (Schaug et al. 1987), CO 120 ppb, methane 1700 ppb, ozone 50 ppb, hydrogen 550 ppb (Simmonds et al. 1996) and formaldehyde 2 ppb (Solberg et al. 1997). Ozone concentrations calculated with the MCMv1.0 in the base case started off at 50 ppb with the air parcel in central Europe and rose to 53 ppb during the first afternoon. On subsequent days, significant ozone production ensued and the mid-afternoon maxima rose from 58 ppb, to 75 ppb, 100 ppb and to 125 ppb on the fifth day, by which time the air parcel had reached the England-Wales border.

2.4 Model Validation

To have confidence in the results concerning ozone formation from industrial hydrocarbon sources, the photochemical trajectory model needs verification and validation over a wide range of species. These validation studies are described briefly in the following paragraphs.

The peak ozone concentration of 125 ppb reached on the fifth day of the base case model experiment can be compared with observations from the UK rural ozone monitoring network for the Aston Hill site in the England-Wales borders. Over the period from 1986-1997, the maximum 1-hour ozone concentration recorded was 125 ppb during 1996 (UK PORG 1997). Previous and subsequent annual maximum values lie in the range 76-110 ppb, illustrating a high degree of year-on-year variability. The base case model experiment produces peak ozone concentrations within a few ppb of those observed during regional scale photochemical ozone episodes.

The adequacy of the model's treatment of VOCs will be a crucial issue in assigning confidence in the model predictions. To this end, the model VOC concentrations have been compared against the observations from the Automatic Hydrocarbon Monitoring Network operated on behalf of DEFRA by AEA Technology (Dollard et al. 1995). The observations of 21 hydrocarbons have been assembled for the month of July 2000 for the rural site at Harwell in Oxfordshire and the mean, maximum and minimum hourly concentrations have been determined. These have been compared with the (logarithm) mean concentrations (in ppb) of each VOC species on the last day of the base case model experiment and the results are shown in Figure 2.1. The observations are shown on a logarithmic scale as the three parallel traces (fine lines) and the model results as the thick line. The VOCs are ordered with increasing elution time in the gas chromatography procedures employed in the observations.

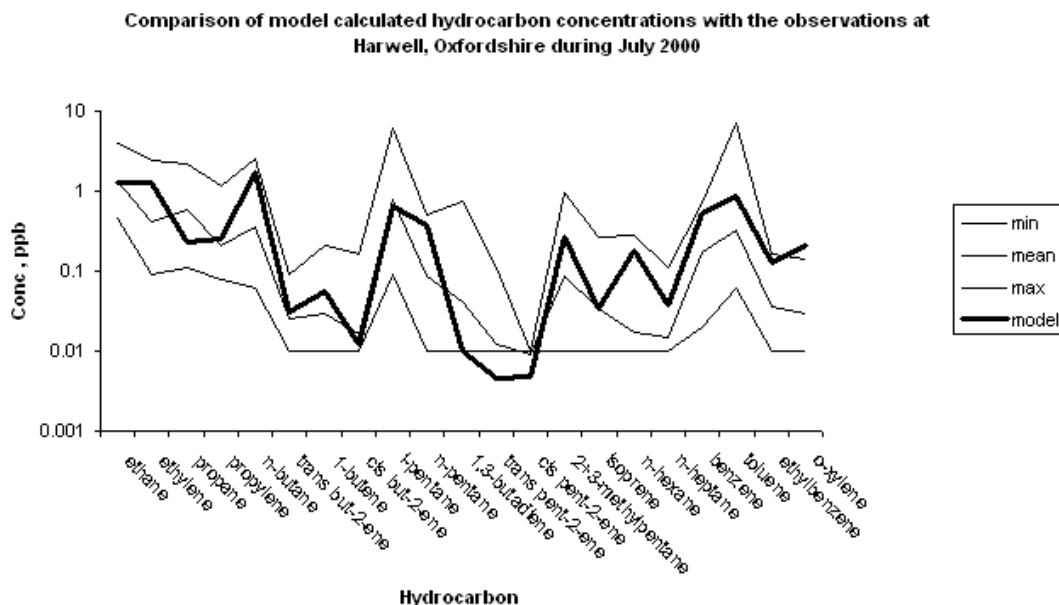


FIGURE 2.1. Comparison of model calculated hydrocarbon concentrations with the observations at Harwell, Oxfordshire during July 2000.

The results of the comparison reveal a similar pattern of concentrations in the observations and model calculations. The peaks and troughs in the three parallel traces are followed closely by the thick model line showing that the model is well able to describe the broad distribution of the VOC classes: alkanes, olefins and aromatics. For the large majority of the VOCs, the model line is close to the mean of the observations. The exceptions are: n-butane, benzene, and ethylbenzene, where the model is close to the maximum in the observations, and cis but-2-ene, 1,3-butadiene, trans pent-2-ene and cis pent-2-ene, where the model is close to the minimum in the observations.

In some respects, the agreement is better than could be expected. This is because the model emissions refer to the base year of 1990 and the observations to the year 2000. In the intervening period, motor vehicle exhaust and fuel evaporative emission controls have been implemented on the European motor vehicle fleet (European Communities 1991) and VOC concentrations are showing marked downwards trends across Europe. Altogether then the level of agreement found in Figure 2.1 across the 21 VOC species between observations and model calculations is considered entirely satisfactory.

In previous work (Derwent et al. 1998), the ozone concentrations calculated in an air parcel travelling along the same five day trajectory with the MCMv1.0, together with a previous version of the mechanism (Derwent et al. 1996), and with the two main chemical mechanisms derived from smog chamber studies, Carbon-Bond IV (Gery et al. 1989) and CAL (Lurmann et al. 1987) were carefully compared together. The ozone concentrations calculated with all four chemical mechanisms agreed closely throughout the five days photochemistry.

Whilst the comparison with ozone observations and the ozone concentrations calculated with other mechanisms demonstrates close agreement, this may not necessarily be the case for other secondary products and free radical intermediates. If the MCMv1.0 can

be shown to give an acceptable description of a series of such species, then this will give a strong indication that the details of the chemistry are being properly represented. Such comparisons have been carried out with observations of the dicarbonyl compounds: glyoxal, methylglyoxal, methacrolein and methylvinylketone (Solberg et al. 1996), with observations of organic hydroperoxides (Hellpointner and Gab 1989; Jackson and Hewitt 1996), organic nitrates (Flocke et al. 1991, 1998; O'Brien et al. 1997), carbonyl compounds (O'Brien et al. 1997), isoprene oxidation products (Williams et al. 1997) and the free radicals: OH, HO₂ and RO₂ (Carslaw, Jacobs and Pilling 1999). With some exceptions, the MCM provides a good description of the ambient data providing some validation of the degradation schemes for the organic compounds and the associated ozone production (Carslaw et al. 1999; Hayman and Jenkin 1999; Jenkin and Hayman 1999; Jenkin et al. 1999).

Testing model performance in the base case situation is necessary, but it fails to answer questions concerning the model's accuracy when it comes to studying the impact of VOC and NO_x controls. Sillman et al. (1997) have devised such tests of model performance, based on a theoretical understanding of the mechanism of photochemical smog formation. They have identified certain particular concentration ratios that provide an indication of whether photochemical ozone has been formed under NO_x-sensitive or VOC-sensitive conditions. A particularly useful indicator ratio is given by the ratio of the concentrations of ozone to oxidised-NO_x, [O₃]/[NO_z], where [NO_z] = [HNO₃] + [PANs] + [nitrate aerosol]. If [O₃]/[NO_z] is less than 10, then ozone formation is VOC-sensitive and if it is greater than 10, then ozone formation is NO_x-sensitive. Predictions of NO_x v VOC sensitivity can be tested by estimating the model ozone responses to 30% reductions in NO_x or VOC emissions.

Figure 2.2 presents the results from a series of 54 model experiments with the UK Photochemical Trajectory Model and the Master Chemical Mechanism. In each case an air parcel was followed over a five day trajectory arriving at a series of grid points 100 km apart across the United Kingdom. Each base case experiment was then repeated with 30% reductions in NO_x and VOC emissions across-the-board. The ozone responses were calculated for each grid point and the pairs of points were plotted against the value of [O₃]/[NO_z] at the trajectory arrival point in the base case model experiment. The ozone responses to 30% VOC control were plotted as open squares and those to 30% NO_x control as + signs. For those grid points with [O₃]/[NO_z] less than 5, the open squares (VOC control) all lay above the y-axis (ozone decreases) and all the + signs (NO_x control) below the axis (ozone increases). For those grid points with [O₃]/[NO_z] greater than 15, all the points were above the y-axis (ozone decreases), but the + signs (NO_x control) were above the open squares (VOC control).

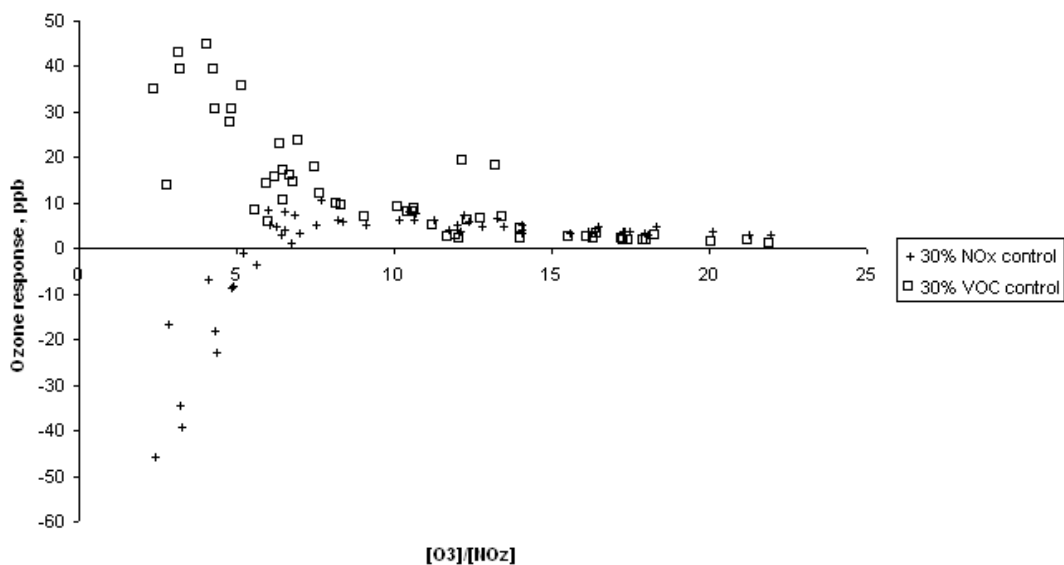


FIGURE 2.2. Comparisons of model ozone responses to changes in NO_x and VOC emission at receptors in all 100km x 100km grid squares across the U.K. as a function of the sensitivity indicator concentration ratio (O₃/NO_z defined in text). The results were calculated using the Master Chemical Mechanism

There is therefore a transition in behaviour between VOC control responses being greater than NO_x responses, to NO_x control responses being greater than VOC responses, as the [O₃]/[NO_z] ratio increases in the UK Photochemical Trajectory Model experiments. This is in accord with the theoretical expectations of Sillman et al. (1997) and this provides strong support for the UK Photochemical Trajectory Model and the Master Chemical Mechanism.

3. MODEL RESULTS

3.1 Estimating Integrated Downwind Ozone Production

In the above base case experiment with the UK Photochemical Trajectory Model, an air parcel is followed over the period of five days as it moves across continental Europe and into the United Kingdom. The model uses the available emission inventories and the MCMv1.0 (Jenkin et al. 1997) to describe regional-scale ozone formation and long-range transport. To describe ozone formation downwind of an industrial source of VOCs, an additional imaginary source is added to the UK VOC emission inventory just as the air parcel enters the United Kingdom. The imaginary VOC source has a constant emission source strength and emits one, and only one, VOC species. No other trace gases are emitted simultaneously with the imaginary industrial source. The source is smeared out over a 10 km x 10 km area and the air parcel takes just under 40 minutes to pass over the source region. These VOC emissions are instantaneously mixed throughout the model atmospheric boundary layer, since no treatment of vertical dispersion, or mixing, is provided in the single-layer trajectory model.

By taking the difference in the ozone concentrations between each model experiment and the base case, at each time point after passing over the imaginary VOC source, the downwind excess ozone formation is quantified, for a given choice of VOC species and emission source strength. The air parcel passes over the imaginary hydrocarbon source during the evening of the **fourth day** and excess downwind ozone concentrations is determined by taking differences from the base case model experiment, throughout the **fifth day**, over a 24 hour period, finishing at 18.00Z. Attention is given both to the peak excess ozone and to the average ozone excess over the 24 hour period.

The excess downwind ozone concentrations have been found to be influenced both by the intrinsic reactivity of the VOC emitted by the industrial source and by the detailed degradation pathway of that VOC species, taking into account any formation of secondary nitrogen compounds which alter the availability of NO_x. With sufficiently large VOC emission rates, ozone excesses become relatively insensitive to further increases in emissions. This is because the peak excess ozone concentration within the air parcel is a property of the base case model experiment. To a first order approximation, this peak excess ozone is dependent on the overall availability of hydroxyl radicals, which is, in turn, controlled by the NO_x levels. Increasing VOC emissions unlocks more and more of this peak excess, until eventually excess ozone begins to level out with increasing VOC emission.

Excess ozone levels in an air parcel downwind of a large industrial source appear to be determined by:

- (a) the VOC emission rate,
- (b) the availability of hydroxyl radicals,
- (c) the reactivity of the VOC compared with the base case reactivity, since this determines the emission rate required for a discernible ozone excess,
- (d) the VOC degradation mechanism and the formation of secondary organic nitrogen compounds.

In the experiments described in this study, the excess downwind ozone concentrations are averaged over the 24-hour period following the time when the air parcel passes over the industrial VOC source. This mean excess ozone concentration is termed the Integrated Downwind Ozone Production (IDOP).

To gauge the potential environmental impact of these ozone excesses, a yardstick of one tenth of the UK air quality standard of 50 ppb (EPAQS 1994), that is 5 ppb, has been used. This is an arbitrary assumption, chosen as a working assumption to complete the analysis. It is an assumption chosen by the user, which if required can be easily replaced and the analysis completed with another assumption. The emission source strength required by each VOC species on its own to generate a mean excess ozone concentration, which equals the yardstick, 5 ppb, is termed the Ozone-equivalent Emission Ceiling (OEC).

The aim of this study has been to estimate the IDOP and OEC values for a wide range of VOC species over a wide range of background conditions.

3.2 Analysis using Future European VOC and NO_x Emissions

In this series of model experiments, the aim has also been to examine the situation when the UN ECE Gothenburg Protocol and the EU National Emissions Ceilings Directive are fully implemented. The question is whether the pattern of photochemical oxidant formation and hence VOC reactivity scales will be changed significantly in the future.

Table 3.1 presents the integrated downwind ozone production (IDOP) values obtained for two VOC source strengths, 0.4 and 10 tonne hour⁻¹, in the base case scenario and with European VOC and NO_x emissions halved. This latter case corresponds reasonably closely to the situation envisaged when the UN ECE Gothenburg Protocol and the EU National Emissions Ceilings Directive are fully implemented. The results show that, broadly speaking, VOC reactivity scales can be defined in both scenarios and that similar rank orders can be assigned to each VOC species in all experiments. The exceptions seem to be the reactive olefins: cis but-2-ene, cis and trans pent-2-ene and cis and trans hex-2-enes, which appear to lose their reactivity entirely in the future emission scenario case.

Table 3.1. Integrated downwind ozone production in ppb for base cases consisting of 0.4 and 10 tonnes per hour of each VOC released at 18.00Z calculated for a background mixture of polluted European air. The calculation is repeated for emissions of 0.4 and 10 tonnes per hour of each VOC released at 18.00Z subject to a background mixture of 50% of the mixture of VOC and NO_x in the base case background air. The table has been displayed, ranking the VOCs according to the ozone production under conditions of a base case release of 0.4 tonnes per hour.

Rank	VOC species	IDOP	IDOP	IDOP	IDOP
		(ppb)	(ppb)	(ppb)	(ppb)
		0.4	10.0	0.4	10.0
		tonne/hr	tonne/hr	tonne/hr	tonne/hr
		base case	base case	50% NO _x & VOC	
1	1,3,5-trimethylbenzene	1.02	13.55	1.15	8.95
2	3,5-dimethylethylbenzene	0.87	12.86	0.95	8.61
3	3,5-diethyltoluene	0.83	12.14	0.88	8.33
4	1,2,4-trimethylbenzene	0.79	11.82	0.87	7.97
5	isoprene	0.78	12.30	0.77	8.66
6	1,2,3-trimethylbenzene	0.74	11.44	0.88	7.81
7	cis but-2-ene	0.69	3.94	0.10	-0.35
8	2-methylbut-2-ene	0.68	2.04	0.61	0.03
9	propylene	0.64	11.91	0.29	6.85
10	but-1-ene	0.58	10.86	0.17	6.37
11	1,3-butadiene	0.56	11.88	0.67	8.79

12 m-xylene	0.55	11.99	0.74	8.71
13 trans pent-2-ene	0.55	3.66	0.07	-0.18
14 ethylene	0.54	13.97	0.08	9.46
15 cis pent-2-ene	0.51	3.66	0.06	-0.18
16 2-methylbut-1-ene	0.47	10.44	0.03	6.94
17 formaldehyde	0.46	11.28	0.66	8.92
18 butylene	0.45	12.12	0.61	10.31
19 p-xylene	0.45	9.60	0.52	7.23
20 trans hex-2-ene	0.44	3.13	0.49	0.68
21 cis hex-2-ene	0.44	3.14	0.47	0.73
22 m-ethyltoluene	0.42	9.46	0.54	7.00
23 3-methylbut-1-ene	0.40	8.73	-0.05	5.11
24 trans but-2-ene	0.39	10.42	0.08	6.66
25 o-xylene	0.38	9.41	0.54	6.88
26 pent-1-ene	0.36	8.40	0.01	4.50
27 i-butyraldehyde	0.28	8.63	0.47	6.31
28 p-ethyltoluene	0.28	7.64	0.42	5.82
29 propionaldehyde	0.27	6.49	0.42	4.78
30 hex-1-ene	0.27	6.93	0.41	4.54
31 o-ethyltoluene	0.16	7.34	0.37	5.55
32 toluene	0.16	5.83	0.23	4.65
33 pentanaldehyde	0.15	5.08	0.27	3.61
34 butyraldehyde	0.13	5.68	0.31	3.98
35 acetaldehyde	0.10	4.51	0.27	3.17
36 ethylbenzene	0.09	6.11	0.29	4.85
37 propylbenzene	0.09	5.17	0.21	4.26
38 i-pentane	0.08	2.57	0.09	2.06
39 n-pentane	0.07	1.97	0.09	1.44
40 i-butane	0.05	2.99	0.15	2.54
41 2-methylpentane	0.04	2.68	0.09	1.95
42 i-butanol	0.03	4.35	0.18	3.65
43 methyl-i-butylketone	0.03	5.61	0.26	4.30
44 methylpropylketone	0.02	3.41	0.17	2.59
45 2,2-dimethylbutane	0.02	1.35	0.04	0.96
46 n-butanol	0.00	3.39	0.14	2.66
47 dimethylether	0.00	2.71	0.10	2.50

48 n-butane	0.00	1.73	0.05	1.37
49 1-methoxy-2-propanol	0.00	3.61	0.17	3.09
50 2-butoxyethanol	0.00	3.89	0.13	3.02
51 methylethylketone	-0.01	2.30	0.09	1.93
52 ethane	-0.02	0.57	0.04	0.47
53 styrene	-0.03	1.20	0.01	-0.37
54 3-methylpentane	-0.03	2.72	0.11	2.06
55 s-butyl acetate	-0.03	2.58	0.09	2.05
56 i-propylbenzene	-0.03	4.97	0.20	3.91
57 n-hexane	-0.04	1.68	0.05	1.00
58 i-propyl acetate	-0.04	2.36	0.06	1.97
59 trans dichloroethylene	-0.06	2.69	0.13	2.50
60 trichloroethylene	-0.06	1.88	0.09	1.71
61 propane	-0.06	1.20	0.06	0.97
62 2-methylhexane	-0.07	1.96	0.06	1.14
63 neopentane	-0.07	1.34	0.07	1.10
64 2,3-dimethylbutane	-0.07	3.13	0.12	2.33
65 3-methylhexane	-0.07	1.85	0.07	1.07
66 cyclohexanol	-0.08	3.53	0.19	2.96
67 methyl-t-butylether	-0.08	1.31	0.03	1.16
68 acetylene	-0.10	0.52	0.02	0.50
69 ethanol	-0.10	1.93	0.06	1.75
70 propanoic acid	-0.12	0.85	0.04	0.83
71 n-decane	-0.12	-0.15	-0.02	-0.66
72 n-octane	-0.12	0.54	0.01	-0.13
73 n-propyl acetate	-0.14	1.94	0.05	1.48
74 n-nonane	-0.14	0.13	-0.01	-0.47
75 s-butanol	-0.14	2.66	0.11	2.32
76 acetone	-0.15	0.51	0.00	0.52
77 cyclohexane	-0.15	2.42	0.07	1.87
78 cis dichloroethylene	-0.15	2.98	0.08	2.76
79 ethyl acetate	-0.15	1.43	0.04	1.20
80 methyl chloride	-0.15	0.04	0.02	0.01
81 n-heptane	-0.15	1.07	0.04	0.44
82 cyclohexanone	-0.16	2.41	0.12	1.85
83 diacetone alcohol	-0.17	1.74	0.09	1.50

84 methylene dichloride	-0.17	0.21	0.01	0.20
85 diethylketone	-0.17	1.99	0.10	1.68
86 formic acid	-0.17	0.33	0.02	0.24
87 methyl chloroform	-0.18	0.11	0.02	0.05
88 n-undecane	-0.18	-0.22	-0.07	-0.86
89 benzene	-0.18	1.88	0.07	1.55
90 tetrachloroethylene	-0.19	0.12	0.01	0.10
91 i-propanol	-0.19	1.71	0.04	1.66
92 n-butyl acetate	-0.20	1.34	0.05	0.90
93 methanol	-0.22	1.21	0.05	1.12
94 acetic acid	-0.22	1.07	0.01	0.94
95 t-butanol	-0.22	1.01	0.02	0.81
96 methyl acetate	-0.24	0.60	0.00	0.49
97 n-dodecane	-0.27	-0.39	-0.09	-0.96
98 benzaldehyde	-0.33	-2.30	-0.21	-3.30
99 methyl-i-propylketone	-0.15	2.59		
100 hexan-2-one	0.11	3.55		
101 hexan-3-one	0.00	2.89		
102 methyl-t-butylketone	-0.06	1.92		
103 n-propanol	0.02	3.01		
104 3-pentanol	-0.13	2.50		
105 2-methylbutanol	0.03	3.43		
106 3-methylbutanol	0.07	4.97		
107 3-methylbutan-2-ol	-0.05	2.88		
108 2-methylbutan-2-ol	-0.12	0.68		
109 ethylene glycol	-0.02	2.98		
110 propylene glycol	0.02	3.50		
111 diethylether	0.22	8.87		
112 diisopropylether	0.26	9.48		
113 ethyl-t-butylether	-0.10	3.54		
114 2-methoxyethanol	0.04	5.21		
115 2-ethoxyethanol	0.08	6.23		
116 1-butoxypropanol	-0.06	3.47		
117 methyl formate	-0.24	0.42		
118 t-butyl acetate	-0.12	0.53		
119 chloroform	-0.18	0.16		

3.3 Changing the time when air parcels pass over the VOC source

Because the atmospheric boundary layer depth varies with time-of-day, an important consideration in the estimation of VOC reactivity scales is when the air parcels pass over the VOC source. In the base case model, the air parcel passes over the VOC source at 18.00Z and the chemical development is followed for a subsequent 24 hours. Shortly after 18.00Z towards dusk, the atmospheric boundary layer collapses from 1300 metres in depth to 300 metres, its night-time level. Emissions then occur into an atmospheric boundary layer with a much reduced depth, producing higher VOC mixing ratios for a given VOC emission source strength. When dawn approaches, the atmospheric boundary layer starts to rise and the hydrocarbon mixing ratios generated by the VOC source begin to decline for a given source strength. Since ozone productivity is related to VOC mixing ratios, the time that the air parcels pass over the VOC source may be an important issue in estimating VOC reactivity scales.

A series of model experiments were performed in which the times that air parcels pass over the VOC source were varied from the base case. The results of these experiments are gathered together in Table 3.2. Each experiment was performed with a VOC source strength of 10 tonne hour⁻¹ and the times that air parcels passed over the source were changed in 6 hour increments. VOC reactivity scales were developed in each case and broadly speaking, the patterns of VOC reactivity remained constant.

Table 3.2. Integrated downwind ozone production in ppb for VOC release of each VOC of 10 tonne/hour for air parcels passing over the industrial source at 18.00Z, 24.00Z, 06.00Z and 12.00Z. The ranking has been determined according the ozone production at 18.00Z. Thus the first column of Table 3.2 is identical to the second column of Table 3.1.

Rank	VOC Species	IDOP	IDOP	IDOP	IDOP
		(ppb)	(ppb)	(ppb)	(ppb)
		18.00Z	24.00Z	06.00Z	12.00Z
	1 ethylene	13.97	21.30	18.61	3.30
	2 1,3,5-trimethylbenzene	13.55	17.20	14.25	1.20
	3 3,5-dimethylethylbenzene	12.86	16.64	13.77	1.09
	4 isoprene	12.30	20.44	17.06	1.42
	5 3,5-diethyltoluene	12.14	16.35	13.53	1.03
	6 butylene	12.12	23.93	20.95	3.38
	7 m-xylene	11.99	17.25	14.36	1.46
	8 propylene	11.91	20.66	18.54	2.28
	9 1,3-butadiene	11.88	19.87	16.86	2.15
	10 1,2,4-trimethylbenzene	11.82	15.76	13.09	1.05
	11 1,2,3-trimethylbenzene	11.44	15.32	12.81	0.96
	12 formaldehyde	11.28	17.73	15.36	2.56
	13 but-1-ene	10.86	18.33	16.29	1.96

14 2-methylbut-1-ene	10.44	20.22	18.37	2.63
15 trans but-2-ene	10.42	14.53	12.45	2.20
16 p-xylene	9.60	14.44	12.14	1.18
17 diisopropylether	9.48		11.44	
18 m-ethyltoluene	9.46	14.06	11.90	1.13
19 o-xylene	9.41	13.98	11.81	0.87
20 diethylether	8.87		10.42	
21 3-methylbut-1-ene	8.73	16.52	15.06	1.37
22 i-butyraldehyde	8.63	12.94	11.56	0.36
23 pent-1-ene	8.40	14.81	13.39	1.28
24 p-ethyltoluene	7.64	11.73	10.14	0.94
25 o-ethyltoluene	7.34	11.04	9.71	0.89
26 hex-1-ene	6.93	12.97	11.66	0.91
27 propionaldehyde	6.49	9.73	8.83	0.07
28 2-ethoxyethanol	6.23		7.52	
29 ethylbenzene	6.11	9.66	8.36	0.95
30 toluene	5.83	9.16	7.94	0.94
31 butyraldehyde	5.68	8.96	8.00	-0.24
32 methyl-i-butylketone	5.61	7.84	7.28	0.75
33 2-methoxyethanol	5.21		6.35	
34 propylbenzene	5.17	8.54	7.39	0.87
35 pentanaldehyde	5.08	8.39	7.45	-0.29
36 i-propylbenzene	4.97	7.90	6.89	0.71
37 3-methylbutanol	4.97		6.72	
38 acetaldehyde	4.51	6.65	6.03	-0.30
39 i-butanol	4.35	6.67	6.07	0.97
40 cis but-2-ene	3.94	11.25	13.73	-0.06
41 2-butoxyethanol	3.89	5.61	5.12	0.80
42 trans pent-2-ene	3.66	9.30	12.99	-0.13
43 cis pent-2-ene	3.66	9.30	12.82	-0.15
44 1-methoxy-2-propanol	3.61	5.23	4.82	0.98
45 hexan-2-one	3.55		4.90	
46 ethyl-t-butylether	3.54		4.31	
47 cyclohexanol	3.53	5.23	4.86	0.78
48 propylene glycol	3.50		4.39	
49 1-butoxypropanol	3.47		4.07	

50 2-methylbutanol	3.43		4.85	
51 methylpropylketone	3.41	5.08	4.69	0.33
52 n-butanol	3.39	4.92	4.49	0.66
53 cis hex-2-ene	3.14	8.43	11.89	-0.39
54 2,3-dimethylbutane	3.13	4.70	4.26	0.55
55 trans hex-2-ene	3.13	8.43	11.89	-0.39
56 n-propanol	3.01		4.06	
57 i-butane	2.99	4.23	3.91	0.86
58 cis dichloroethylene	2.98	4.27	3.93	0.86
59 ethylene glycol	2.98		4.17	
60 hexan-3-one	2.89		4.05	
61 3-methylbutan-2-ol	2.88		3.93	
62 3-methylpentane	2.72	3.87	3.60	0.62
63 dimethylether	2.71	3.75	3.54	1.01
64 trans dichloroethylene	2.69	3.90	3.58	0.79
65 2-methylpentane	2.68	3.84	3.53	0.53
66 s-butanol	2.66	3.84	3.59	0.76
67 methyl-i-propylketone	2.59		3.76	
68 s-butyl acetate	2.58	3.73	3.48	0.68
69 i-pentane	2.57	3.62	3.37	0.68
70 3-pentanol	2.50		3.51	
71 cyclohexane	2.42	3.56	3.37	0.62
72 cyclohexanone	2.41	3.49	3.29	0.54
73 i-propyl acetate	2.36	3.40	3.19	0.68
74 methylethylketone	2.30	3.80	3.53	0.31
75 2-methylbut-2-ene	2.04	8.92	12.46	-0.94
76 diethylketone	1.99	3.15	2.94	0.28
77 n-pentane	1.97	2.79	2.61	0.47
78 2-methylhexane	1.96	2.86	2.66	0.28
79 n-propyl acetate	1.94	2.66	2.48	0.48
80 ethanol	1.93	2.83	2.65	0.45
81 methyl-t-butylketone	1.92		2.94	
82 trichloroethylene	1.88	2.66	2.47	0.57
83 benzene	1.88	2.74	2.55	0.47
84 3-methylhexane	1.85	2.75	2.54	0.23
85 diacetone alcohol	1.74	2.97	2.74	0.28

86 n-butane	1.73	2.42	2.27	0.49
87 i-propanol	1.71	2.61	2.44	0.61
88 n-hexane	1.68	2.44	2.25	0.30
89 ethyl acetate	1.43	2.04	1.92	0.40
90 2,2-dimethylbutane	1.35	2.02	1.87	0.30
91 n-butyl acetate	1.34	2.00	1.86	0.30
92 neopentane	1.34	1.94	1.79	0.40
93 methyl-t-butylether	1.31	1.92	1.80	0.41
94 methanol	1.21	1.86	1.75	0.40
95 styrene	1.20	5.89	6.58	0.39
96 propane	1.20	1.68	1.58	0.41
97 n-heptane	1.07	1.67	1.54	0.09
98 acetic acid	1.07	1.43	1.33	0.38
99 t-butanol	1.01	1.38	1.32	0.31
100 propanoic acid	0.85	1.28	1.22	0.32
101 2-methylbutan-2-ol	0.68		1.04	
102 methyl acetate	0.60	0.79	0.75	0.21
103 ethane	0.57	0.76	0.71	0.21
104 n-octane	0.54	0.91	0.84	-0.11
105 t-butyl acetate	0.53		0.74	
106 acetylene	0.52	0.87	0.78	0.19
107 acetone	0.51	0.94	0.91	0.16
108 methyl formate	0.42		0.44	
109 formic acid	0.33	0.37	0.37	0.14
110 methylene dichloride	0.21	0.33	0.34	0.13
111 chloroform	0.16		0.19	
112 n-nonane	0.13	0.41	0.36	-0.24
113 tetrachloroethylene	0.12	0.20	0.18	0.10
114 methyl chloroform	0.11	0.16	0.17	0.10
115 methyl chloride	0.04	0.07	0.08	0.07
116 n-decane	-0.15	0.11	0.08	-0.33
117 n-undecane	-0.22	-0.09	-0.11	-0.42
118 n-dodecane	-0.39	-0.28	-0.28	-0.49
119 benzaldehyde	-2.30	-2.10	-2.43	-1.63

3.4 Mixtures of VOCs v single VOC species

In the above experiments, the reactivity scales have been estimated by emitting a single VOC species and estimating the integrated downwind ozone production. Clearly each VOC species competes against the mix of VOC species and this competition is measured in the reactivity scale. However there remains the possibility that the combination of two VOC species together may stimulate ozone productivity rather than compete against each other, and this hypothesis is tested in a series of model experiments. In this series of experiments, the VOC source is assumed to be emitting 10 tonne hour⁻¹ of ethylene and 10 tonne hour⁻¹ of an additional VOC species, taken one at a time.

Table 3.3 presents the results of the model experiments using mixtures of VOC species. The results for ethylene show the expected competition between the VOC species since the majority of the entries are negative. That is to say, the presence of the additional VOC species reduces the integrated downwind ozone production from the ethylene. In a relatively small number of cases, a positive entry is shown in Table 3, reflecting some form of synergy, or heightened ozone productivity. Broadly speaking these heightened ozone productivities are rather small and are induced by relatively unreactive VOC species.

Table 3.3. Influence on the integrated downwind ozone production in ppb from 10 tonnes/hour ethylene emitted at the same time as an emission of another VOC at 10 tonnes/hour

VOC species	Change in IDOP (ppb)
ethane	-0.4
propane	-0.1
n-butane	-1.9
i-butane	1.8
n-pentane	-3.5
i-pentane	-2.1
n-hexane	-6.9
2-methylpentane	-4.3
3-methylpentane	-4.2
2,2-dimethylbutane	-2.6
2,3-dimethylbutane	-4.6
n-heptane	-9.5
2-methylhexane	-6.7
3-methylhexane	-7.4
n-octane	-11.6
neopentane	0.4

n-nonane	-12.9
n-decane	-13.2
n-undecane	-13.4
n-dodecane	-12.8
propylene	-28.2
but-1-ene	-23.7
cis but-2-ene	-58.5
trans but-2-ene	-17.7
cis pent-2-ene	-56.8
trans pent-2-ene	-56.7
pent-1-ene	-25.5
2-methylbut-1-ene	-28.6
3-methylbut-1-ene	-28.9
2-methylbut-2-ene	-67.5
butylene	-26.5
acetylene	0.0
benzene	0.7
toluene	-5.7
o-xylene	-18.3
m-xylene	-15.2
p-xylene	-12.7
ethylbenzene	-5.6
propylbenzene	0.0
i-propylbenzene	-5.0
1,2,3-trimethylbenzene	-20.5
1,2,4-trimethylbenzene	-19.8
1,3,5-trimethylbenzene	-22.0
o-ethyltoluene	-9.9
m-ethyltoluene	-12.5
p-ethyltoluene	-9.4
formaldehyde	12.4
acetaldehyde	-32.5
propionaldehyde	-28.0
butyraldehyde	-30.4
i-butyraldehyde	-26.0
pentanaldehyde	-31.0

benzaldehyde	-43.1
acetone	-2.9
methylethylketone	-13.9
methyl-i-butylketone	-19.1
methanol	1.2
ethanol	-4.5
methyl acetate	0.1
ethyl acetate	-1.1
i-propyl acetate	1.2
n-butyl acetate	-3.7
s-butyl acetate	-0.2
methylene dichloride	-0.1
methyl chloride	0.0
tetrachloroethylene	0.1
trichloroethylene	1.6
cyclohexane	-0.9
styrene	-40.3
n-butanol	-6.8
diacetone alcohol	-8.0
formic acid	0.3
acetic acid	1.3
methyl chloroform	0.0
cis dichloroethylene	2.6
i-propanol	1.5
i-butanol	-2.5
s-butanol	-1.4
cyclohexane	-1.8
cyclohexanol	-4.1
2-butoxyethanol	-7.3
1-methoxy-2-propanol	-3.4
3,5- dimethylethylbenzene	-21.1
3,5-diethyltoluene	-20.0
isoprene	-42.2
t-butanol	0.5
dimethylether	3.8
methyl-t-butylether	-0.9

n-propyl acetate	-2.5
trans dichloroethylene	2.3
propanoic acid	-0.6
hex-1-ene	-26.9
cis hex-2-ene	-54.4
trans hex-2-ene	-54.4
1,3-butadiene	-30.0
methylpropylketone	-18.8

3.5 Influence of simultaneous NO_x emissions

In all of the above experiments, reactivity scales have been developed for idealised cases in which single VOC species, or simple mixtures of VOC species, have been emitted into a photochemically reacting air mass. There remains the possibility that the oxidation of the additional VOC species, or the components of its mixtures, may have depleted the available NO_x and hence ozone productivity may have been less than the maximum possible. In the following series of experiments, the VOC source was assumed to be emitting 10 tonne hour⁻¹ as before, but now with 10 tonne hour⁻¹ NO_x emitted simultaneously to reduce to a minimum any NO_x inhibition due to lack of availability of NO_x.

Table 3.4 presents the results of the model experiment with simultaneous NO_x and VOC emissions for air parcels passing over the source at 06.00Z. The increased availability made a dramatic difference to the integrated downwind ozone concentrations compared to the case without simultaneous NO_x emission (see Table 2). For the 50 or so most reactive VOC species in Table 3.4, the integrated downwind ozone production estimates were about a factor of four higher with the simultaneous NO_x emission compared to the case without. For these species, the ozone production is roughly in proportion, with and without simultaneous NO_x emissions, also showing that the reactivity scales are similar in terms of relative rankings.

For the remaining 50 or so VOC species, this factor of four enhancement in the integrated downwind ozone production was not seen and the relative enhancement dropped off quickly with decreasing reactivity. For the highly unreactive species, there is no enhancement in the IDOP, and the IDOP sometimes becomes negative. Under these conditions, the slight increase in ozone production from the unreactive VOC species had not been enough to counteract the effect of the increased NO_x emission.

Table 3.4. Integrated downwind ozone production in ppb for the emission of 10 tonne/hr of each VOC species in the base case and simultaneous NO_x cases for an emission plume at 06.00Z. The base case is identical to the third column of Table 3.2. The ordering has been chosen according to the ozone production.

Rank	VOC species	IDOP (ppb)	IDOP (ppb)
		Base case	Simultaneous NO _x case
1	ethylene	18.61	87.80
2	butylene	20.95	82.80
3	formaldehyde	15.36	78.34
4	diisopropylether	11.44	67.06
5	2-methylbut-1-ene	18.37	66.81
6	diethylether	10.42	60.26
7	trans but-2-ene	12.45	56.00
8	m-xylene	14.36	55.15
9	but-1-ene	16.29	52.14
10	1,3-butadiene	16.86	52.13
11	1,3,5-trimethylbenzene	14.25	50.87
12	3,5-diethyltoluene	13.53	50.40
13	3,5-dimethylethylbenzene	13.77	50.21
14	p-xylene	12.14	49.98
15	m-ethyltoluene	11.90	49.58
16	propylene	18.54	49.01
17	1,2,4-trimethylbenzene	13.09	48.22
18	1,2,3-trimethylbenzene	12.81	46.84
19	3-methylbut-1-ene	15.06	46.35
20	pent-1-ene	13.39	46.17
21	p-ethyltoluene	10.14	45.13
22	o-xylene	11.81	44.67
23	hex-1-ene	11.66	43.55
24	o-ethyltoluene	9.71	43.29
25	ethylbenzene	8.36	42.58
26	i-butyraldehyde	11.56	41.80
27	propylbenzene	7.39	41.74
28	toluene	7.94	40.97
29	2-ethoxyethanol	7.52	40.80

30 i-propylbenzene	6.89	36.68
31 propionaldehyde	8.83	36.49
32 isoprene	17.06	36.24
33 methyl-i-butylketone	7.28	35.37
34 3-methylbutanol	6.72	35.33
35 pentanaldehyde	7.45	34.98
36 butyraldehyde	8.00	33.60
37 i-butanol	6.07	33.49
38 2-methoxyethanol	6.35	33.21
39 acetaldehyde	6.03	27.53
40 styrene	6.58	26.99
41 hexan-2-one	4.90	25.37
42 2-methylbutanol	4.85	25.02
43 methylpropylketone	4.69	24.05
44 propylene glycol	4.39	22.16
45 ethylene glycol	4.17	21.40
46 cis dichloroethylene	3.93	21.13
47 2-butoxyethanol	5.12	20.08
48 hexan-3-one	4.05	19.93
49 n-butanol	4.49	19.69
50 methyl-i-propylketone	3.76	18.85
51 2,3-dimethylbutane	4.26	18.77
52 methylethylketone	3.53	17.63
53 ethyl-t-butylether	4.31	16.76
54 trans dichloroethylene	3.58	16.35
55 cis hex-2-ene	11.89	14.68
56 trans hex-2-ene	11.89	14.68
57 n-propanol	4.06	14.17
58 methyl-t-butylketone	2.94	13.70
59 cyclohexanol	4.86	13.31
60 trans pent-2-ene	12.99	13.26
61 1-methoxy-2-propanol	4.82	13.13
62 cis pent-2-ene	12.82	12.94
63 diacetone alcohol	2.74	11.68
64 cis but-2-ene	13.73	11.17
65 diethylketone	2.94	10.54

66 i-butane	3.91	10.26
67 3-methylbutan-2-ol	3.93	7.75
68 s-butyl acetate	3.48	7.00
69 1-butoxypropanol	4.07	6.77
70 2-methylbut-2-ene	12.46	6.76
71 2-methylpentane	3.53	6.40
72 s-butanol	3.59	5.30
73 3-pentanol	3.51	4.53
74 3-methylpentane	3.60	3.85
75 i-propyl acetate	3.19	3.66
76 cyclohexanone	3.29	2.19
77 i-pentane	3.37	1.11
78 trichloroethylene	2.47	0.05
79 benzene	2.55	-0.66
80 3-methylhexane	2.54	-1.24
81 benzaldehyde	-2.43	-1.73
82 ethanol	2.65	-1.93
83 cyclohexane	3.37	-2.10
84 n-propyl acetate	2.48	-2.11
85 2-methylhexane	2.66	-2.87
86 dimethylether	3.54	-3.02
87 n-pentane	2.61	-3.81
88 2,2-dimethylbutane	1.87	-4.81
89 n-hexane	2.25	-5.05
90 i-propanol	2.44	-5.44
91 n-butyl acetate	1.86	-5.61
92 n-butane	2.27	-5.74
93 ethyl acetate	1.92	-7.39
94 methanol	1.75	-7.74
95 neopentane	1.79	-7.87
96 n-heptane	1.54	-8.42
97 methyl-t-butylether	1.80	-9.73
98 acetone	0.91	-9.76
99 propane	1.58	-10.42
100 n-octane	0.84	-10.50
101 t-butanol	1.32	-11.35

102 n-nonane	0.36	-11.76
103 acetic acid	1.33	-12.07
104 n-decane	0.08	-12.36
105 propanoic acid	1.22	-12.54
106 2-methylbutan-2-ol	1.04	-12.59
107 n-undecane	-0.11	-12.67
108 n-dodecane	-0.28	-12.96
109 acetylene	0.78	-13.57
110 t-butyl acetate	0.74	-14.15
111 methyl acetate	0.75	-14.48
112 ethane	0.71	-14.67
113 methyl formate	0.44	-15.87
114 formic acid	0.37	-16.07
115 methylene dichloride	0.34	-16.10
116 tetrachloroethylene	0.18	-16.64
117 chloroform	0.19	-16.65
118 methyl chloroform	0.17	-16.79
119 methyl chloride	0.08	-17.08

Amongst the VOCs which are reactive in the base case, there are 6 VOC species which showed little or no enhancement between Tables 3.2 and 3.4 due to simultaneous NO_x emission. These species are: 2-methylbut-2-ene, cis but-2-ene, cis and trans pent-2-enes and cis and trans hex-2-enes. These are easily identified as the species with IDOP > 10 in the base case, but little change in the simultaneous NO_x case. These species are all considered highly reactive and it is surprising that they have not shown the order of magnitude enhancement. Although these species are highly reactive with OH radicals and were able to stimulate additional ozone production, they also react rapidly with ozone itself, leading to ozone destruction, which limited ultimately their apparent enhancements due to simultaneous NO_x emission.

3.6 Influence of London's Emissions

As a variant on the above scenario case with simultaneous NO_x emissions, the path taken by the air parcel before reaching the imaginary industrial VOC source was changed so that the air parcel had passed over the London conurbation. In this way, the VOC and NO_x precursor concentrations in the air parcel, immediately prior to receiving the emissions from the imaginary source, were dramatically different from those in the base case.

Table 3.5 presents the results of the model experiment for an air parcel passing over London before the imaginary industrial VOC source. The integrated downwind ozone concentration increments were about a factor of two to three higher than those in the base case for the same conditions of a 10 tonne hour⁻¹ source at 06.00Z. The integrated

downwind ozone increments were enhanced by the almost the same factor for almost all of the VOC species studied. When the IDOP is very small, it is not reported.

Table 3.5. Integrated downwind ozone production in ppb for the emission of 10 tonnes/hour of each VOC species in an emission plume at 06.00Z in an air parcel which has been modified by previously passing over London.

Rank VOC species	IDOP	IDOP
	(ppb)	(ppb)
	Base case	London case
1 cis but-2-ene	13.73	48.40
2 cis pent-2-ene	12.82	44.46
3 trans pent-2-ene	12.99	44.44
4 1,3,5-trimethylbenzene	14.25	43.57
5 2-methylbut-2-ene	12.46	41.52
6 3,5-dimethylethylbenzene	13.77	41.23
7 propylene	18.54	40.40
8 isoprene	17.06	40.27
9 cis hex-2-ene	11.89	39.95
10 trans hex-2-ene	11.89	39.95
11 3,5-diethyltoluene	13.53	39.25
12 1,2,4-trimethylbenzene	13.09	37.61
13 1,2,3-trimethylbenzene	12.81	37.25
14 butylene	20.95	34.91
15 but-1-ene	16.29	34.52
16 1,3-butadiene	16.86	34.26
17 m-xylene	14.36	34.14
18 2-methylbut-1-ene	18.37	32.68
19 3-methylbut-1-ene	15.06	32.45
20 formaldehyde	15.36	29.24
21 pent-1-ene	13.39	28.94
22 ethylene	18.61	28.03
23 o-xylene	11.81	27.47
24 m-ethyltoluene	11.90	26.63
25 p-xylene	12.14	26.57
26 i-butyraldehyde	11.56	25.48

27 hex-1-ene	11.66	25.03
28 propionaldehyde	8.83	23.63
29 trans but-2-ene	12.45	23.46
30 butyraldehyde	8.00	21.98
31 p-ethyltoluene	10.14	20.34
32 pentanaldehyde	7.45	19.91
33 o-ethyltoluene	9.71	18.93
34 styrene	6.58	17.32
35 acetaldehyde	6.03	17.28
36 methyl-i-butylketone	7.28	13.65
37 ethylbenzene	8.36	12.32
38 toluene	7.94	11.25
39 propylbenzene	7.39	9.78
40 i-propylbenzene	6.89	9.26
41 methylpropylketone	4.69	9.24
42 i-butanol	6.07	6.84
43 methylethylketone	3.53	6.32
44 2-butoxyethanol	5.12	5.35
45 n-butanol	4.49	5.26
46 2,3-dimethylbutane	4.26	5.01
47 cyclohexanol	4.86	4.83
48 benzaldehyde	-2.43	4.53
49 diacetone alcohol	2.74	4.37
50 1-methoxy-2-propanol	4.82	4.20
51 2-methylpentane	3.53	3.35
52 3-methylpentane	3.60	3.13
53 cis dichloroethylene	3.93	2.88
54 s-butanol	3.59	2.78
55 3-methylhexane	2.54	2.69
56 cyclohexanone	3.29	2.68
57 i-butane	3.91	2.67
58 s-butyl acetate	3.48	2.62
59 trans dichloroethylene	3.58	2.55
60 i-pentane	3.37	2.50
61 2-methylhexane	2.66	2.48
62 cyclohexane	3.37	2.18

63 i-propyl acetate	3.19	2.13
64 n-hexane	2.25	2.04
65 ethanol	2.65	2.02
66 n-pentane	2.61	1.99
67 n-propyl acetate	2.48	1.84
68 dimethylether	3.54	1.76
69 benzene	2.55	1.66
70 trichloroethylene	2.47	1.62
71 2,2-dimethylbutane	1.87	1.56
72 n-heptane	1.54	1.56
73 n-butyl acetate	1.86	1.53
74 n-butane	2.27	1.52
75 i-propanol	2.44	1.40
76 n-octane	0.84	1.19
77 ethyl acetate	1.92	1.18
78 acetone	0.91	1.10
79 neopentane	1.79	1.06
80 methanol	1.75	1.00
81 methyl-t-butylether	1.80	0.96
82 n-nonane	0.36	0.89
83 propane	1.58	0.82
84 n-decane	0.08	0.73
85 t-butanol	1.32	0.67
86 n-undecane	-0.11	0.64
87 acetic acid	1.33	0.58
88 n-dodecane	-0.28	0.57
89 propanoic acid	1.22	0.54
90 acetylene	0.78	0.41
91 methyl acetate	0.75	0.28
92 methylene dichloride	0.34	0.02
93 formic acid	0.37	0.01
94 ethane	0.71	0.00
95 diethylketone	2.94	0.00
97 methyl-i-propylketone	3.76	0.00
98 tetrachloroethylene	0.18	-0.06
99 methyl chloroform	0.17	-0.09

100 methyl chloride	0.08	-0.14
101 hexan-2-one	4.90	
102 hexan-3-one	4.05	
103 methyl-t-butylketone	2.94	
104 n-propanol	4.06	
105 3-pentanol	3.51	
106 2-methylbutanol	4.85	
107 3-methylbutanol	6.72	
108 3-methylbutan-2-ol	3.93	
109 2-methylbutan-2-ol	1.04	
110 ethylene glycol	4.17	
111 propylene glycol	4.39	
112 diethylether	10.42	
113 diisopropylether	11.44	
114 ethyl-t-butylether	4.31	
115 2-methoxyethanol	6.35	
116 2-ethoxyethanol	7.52	
117 1-butoxypropanol	4.07	
118 methyl formate	0.44	
119 t-butyl acetate	0.74	
120 chloroform	0.19	

3.7 A High Isoprene Emission Case

As a variant on the base case scenario, which employs EMEP estimates of isoprene emissions across Europe, a high isoprene case was formulated by including significantly higher emissions. Instead of a spatially varying isoprene emission field, isoprene emissions were set at a constant rate using the maximum isoprene emission rate found in the United Kingdom.

Table 3.6 presents the integrated downwind ozone production estimates in ppb for the base case and high isoprene case, each having an emission of 10 tonne/hour of each VOC species at 06.00Z. Clearly the assumptions concerning isoprene emissions make only a small difference to the ozone production estimates, particularly for the most reactive VOC species. However as reactivity declines, some differences in downwind ozone production become apparent between the base case and high isoprene case. Differences are generally of little significance except for particular oxygenated VOC species: diisopropylether, diethylether, 2-ethoxyethanol, 3-methylbutanol, 2-methoxyethanol, hexan-2-one, 2-methylbutanol, ethyl-t-butylether, ethylene glycol, 1-butoxypropanol, n-propanol, 3-methylbutan-2-ol, methyl-i-propylketone, diethylketone and 2-methylbutan-2-ol. There is clearly an interaction occurring here between the

isoprene and oxygenate chemical mechanisms and this is the subject of further investigation.

Table 3.6. Integrated downwind ozone production in ppb for the emission of 10 tonne/hour of each VOC species at 06:00Z in the base case and in the high isoprene case.

Rank VOC species	IDOP (ppb)	IDOP (ppb)
	Base case	High isoprene case
1 butylene	20.95	20.57
2 ethylene	18.61	18.39
3 propylene	18.54	18.14
4 2-methylbut-1-ene	18.37	18.10
5 isoprene	17.06	16.50
6 1,3-butadiene	16.86	16.39
7 but-1-ene	16.29	15.93
8 formaldehyde	15.36	15.09
9 3-methylbut-1-ene	15.06	14.71
10 m-xylene	14.36	14.12
11 1,3,5-trimethylbenzene	14.25	13.83
12 3,5-dimethylethylbenzene	13.77	13.32
13 cis but-2-ene	13.73	13.19
14 3,5-diethyltoluene	13.53	13.04
15 pent-1-ene	13.39	13.06
16 1,2,4-trimethylbenzene	13.09	12.74
17 trans pent-2-ene	12.99	12.46
18 cis pent-2-ene	12.82	12.40
19 1,2,3-trimethylbenzene	12.81	12.49
20 2-methylbut-2-ene	12.46	11.97
21 trans but-2-ene	12.45	12.19
22 p-xylene	12.14	11.90
23 m-ethyltoluene	11.90	11.66
24 cis hex-2-ene	11.89	11.41
25 trans hex-2-ene	11.89	11.41
26 o-xylene	11.81	11.47
27 hex-1-ene	11.66	11.35

28 i-butyraldehyde	11.56	11.16
29 diisopropylether	11.44	10.31
30 diethylether	10.42	4.27
31 p-ethyltoluene	10.14	9.82
32 o-ethyltoluene	9.71	9.43
33 propionaldehyde	8.83	8.46
34 ethylbenzene	8.36	8.20
35 butyraldehyde	8.00	7.59
36 toluene	7.94	7.77
37 2-ethoxyethanol	7.52	6.22
38 pentanaldehyde	7.45	7.08
39 propylbenzene	7.39	7.26
40 methyl-i-butylketone	7.28	7.07
41 i-propylbenzene	6.89	6.71
42 3-methylbutanol	6.72	4.73
43 styrene	6.58	6.27
44 2-methoxyethanol	6.35	4.21
45 i-butanol	6.07	5.92
46 acetaldehyde	6.03	5.72
47 2-butoxyethanol	5.12	5.03
48 hexan-2-one	4.90	3.61
49 cyclohexanol	4.86	4.78
50 2-methylbutanol	4.85	3.42
51 1-methoxy-2-propanol	4.82	4.71
52 methylpropylketone	4.69	4.50
53 n-butanol	4.49	4.38
54 propylene glycol	4.39	4.06
55 ethyl-t-butylether	4.31	11.29
56 2,3-dimethylbutane	4.26	4.20
57 ethylene glycol	4.17	0.98
58 1-butoxypropanol	4.07	7.39
59 n-propanol	4.06	2.79
60 hexan-3-one	4.05	4.70
61 cis dichloroethylene	3.93	3.85
62 3-methylbutan-2-ol	3.93	6.57
63 i-butane	3.91	3.87

64 methyl-i-propylketone	3.76	2.80
65 3-methylpentane	3.60	3.53
66 s-butanol	3.59	3.48
67 trans dichloroethylene	3.58	3.51
68 dimethylether	3.54	3.51
69 2-methylpentane	3.53	3.49
70 methylethylketone	3.53	3.37
71 3-pentanol	3.51	3.93
72 s-butyl acetate	3.48	3.41
73 i-pentane	3.37	3.34
74 cyclohexane	3.37	3.33
75 cyclohexanone	3.29	3.23
76 i-propyl acetate	3.19	3.11
77 methyl-t-butylketone	2.94	3.86
78 diethylketone	2.94	4.47
79 diacetone alcohol	2.74	2.60
80 2-methylhexane	2.66	2.61
81 ethanol	2.65	2.57
82 n-pentane	2.61	2.58
83 benzene	2.55	2.50
84 3-methylhexane	2.54	2.50
85 n-propyl acetate	2.48	2.41
86 trichloroethylene	2.47	2.37
87 i-propanol	2.44	2.38
88 n-butane	2.27	2.22
89 n-hexane	2.25	2.24
90 ethyl acetate	1.92	1.84
91 2,2-dimethylbutane	1.87	1.81
92 n-butyl acetate	1.86	1.78
93 methyl-t-butylether	1.80	1.74
94 neopentane	1.79	1.74
95 methanol	1.75	1.68
96 propane	1.58	1.56
97 n-heptane	1.54	1.51
98 acetic acid	1.33	1.29
99 t-butanol	1.32	1.25

100 propanoic acid	1.22	1.16
101 2-methylbutan-2-ol	1.04	3.83
102 acetone	0.91	0.82
103 n-octane	0.84	0.81
104 acetylene	0.78	0.74
105 methyl acetate	0.75	0.69
106 t-butyl acetate	0.74	0.37
107 ethane	0.71	0.64
108 methyl formate	0.44	4.00
109 formic acid	0.37	0.30
110 n-nonane	0.36	0.34
111 methylene dichloride	0.34	0.27
112 chloroform	0.19	0.68
113 tetrachloroethylene	0.18	0.13
114 methyl chloroform	0.17	0.10
115 methyl chloride	0.08	0.03
116 n-decane	0.08	0.08
117 n-undecane	-0.11	-0.12
118 n-dodecane	-0.28	-0.31
119 benzaldehyde	-2.43	-2.61

4. DEVELOPMENT OF OZONE IMPACT INDEX FOR VOCs

In this study, a wide range of sensitivity experiments were performed which aimed to quantify the integrated downwind ozone production (IDOP) following the emission of an individual VOC species from an imaginary industrial VOC source. The relationship between integrated downwind ozone production and VOC emission source strength has previously been found to be non-linear, with a slope that decreases with increasing VOC emission source strength. The range of sensitivity studies performed was examined to find the maximum integrated downwind ozone production (maximum IDOP) in ppb per VOC emission rate in tonne hour⁻¹. This quantity is tabulated in Table 4.1 for each VOC species studied across the complete range of sensitivity studies performed.

Accepting a maximum ozone increment of 5 ppb downwind of the industrial source, then the emission rate of each VOC species in tonne hour⁻¹ that would just generate this increment could be determined. This is the ozone-equivalent emission ceiling (OEC). The corresponding OEC values were determined for each VOC studied and the values are also tabulated in Table 4.1. The ozone-equivalent emission ceilings varied from 0.6 tonne hour⁻¹ for the most reactive species: ethylene and butylene, to about 150 tonne hour⁻¹ for the least reactive species: methylene dichloride. Table 4.1 represents the best precautionary estimates of the ozone production in the downwind environment, which are a step towards a method for use within a regulatory framework. The method would replace photochemical ozone creation potentials, because the latter only describes emission equivalence. In the following section issues associated with the application of the methods are discussed.

Table 4.1. Integrated downwind ozone production in ppb per tonne/hour and the ozone-equivalent emission ceilings in tonnes/hour for each VOC based on an overall ranking determined by the maximum ozone production per tonne of VOC released

Rank	VOC species	IDOP per tonne/hour	OEC
		Integrated downwind ozone production in ppb per tonne/hour	Ozone emission ceiling in tonnes /hour
1	ethylene	8.78	0.57
2	butylene	8.28	0.60
3	formaldehyde	7.83	0.64
4	diisopropylether	6.71	0.75
5	2-methylbut-1-ene	6.68	0.75
6	diethylether	6.03	0.83
7	trans but-2-ene	5.60	0.89

8 m-xylene	5.52	0.91
9 but-1-ene	5.21	0.96
10 1,3-butadiene	5.21	0.96
11 1,3,5-trimethylbenzene	5.09	0.98
12 3,5-diethyltoluene	5.04	0.99
13 3,5-dimethylethylbenzene	5.02	1.00
14 p-xylene	5.00	1.00
15 m-ethyltoluene	4.96	1.01
16 propylene	4.90	1.02
17 cis but-2-ene	4.84	1.03
18 1,2,4-trimethylbenzene	4.82	1.04
19 1,2,3-trimethylbenzene	4.68	1.07
20 3-methylbut-1-ene	4.64	1.08
21 pent-1-ene	4.62	1.08
22 p-ethyltoluene	4.51	1.11
23 o-xylene	4.47	1.12
24 cis pent-2-ene	4.45	1.12
25 trans pent-2-ene	4.44	1.13
26 hex-1-ene	4.36	1.15
27 o-ethyltoluene	4.33	1.15
28 ethylbenzene	4.26	1.17
29 i-butyraldehyde	4.18	1.20
30 propylbenzene	4.17	1.20
31 2-methylbut-2-ene	4.15	1.20
32 toluene	4.10	1.22
33 2-ethoxyethanol	4.08	1.23
34 isoprene	4.03	1.24
35 cis hex-2-ene	4.00	1.25
36 trans hex-2-ene	4.00	1.25
37 i-propylbenzene	3.67	1.36
38 propionaldehyde	3.65	1.37
39 methyl-i-butylketone	3.54	1.41
40 3-methylbutanol	3.53	1.42
41 pentanaldehyde	3.50	1.43
42 butyraldehyde	3.36	1.49
43 i-butanol	3.35	1.49

44 2-methoxyethanol	3.32	1.51
45 acetaldehyde	2.75	1.82
46 styrene	2.70	1.85
47 hexan-2-one	2.54	1.97
48 2-methylbutanol	2.50	2.00
49 methylpropylketone	2.40	2.08
50 propylene glycol	2.22	2.26
51 ethylene glycol	2.14	2.34
52 cis dichloroethylene	2.11	2.37
53 2-butoxyethanol	2.01	2.49
54 hexan-3-one	1.99	2.51
55 n-butanol	1.97	2.54
56 methyl-i-propylketone	1.89	2.65
57 2,3-dimethylbutane	1.88	2.66
58 methylethylketone	1.76	2.84
59 ethyl-t-butylether	1.68	2.98
60 trans dichloroethylene	1.64	3.06
61 n-propanol	1.42	3.53
62 methyl-t-butylketone	1.37	3.65
63 cyclohexanol	1.33	3.76
64 1-methoxy-2-propanol	1.31	3.81
65 diacetone alcohol	1.17	4.28
66 diethylketone	1.05	4.74
67 i-butane	1.03	4.87
68 3-methylbutan-2-ol	0.78	6.45
69 1-butoxypropanol	0.74	6.76
70 s-butyl acetate	0.70	7.14
71 2-methylpentane	0.64	7.81
72 s-butanol	0.53	9.44
73 benzaldehyde	0.45	11.04
74 3-pentanol	0.45	11.04
75 methyl formate	0.40	12.49
76 3-methylpentane	0.39	12.92
77 2-methylbutan-2-ol	0.38	13.06
78 dimethylether	0.38	13.32
79 i-propyl acetate	0.37	13.67

80 i-pentane	0.36	13.83
81 cyclohexane	0.36	14.04
82 cyclohexanone	0.35	14.32
83 2-methylhexane	0.29	17.47
84 ethanol	0.28	17.69
85 n-pentane	0.28	17.93
86 3-methylhexane	0.27	18.20
87 benzene	0.27	18.24
88 trichloroethylene	0.27	18.78
89 n-propyl acetate	0.27	18.82
90 i-propanol	0.26	19.16
91 n-hexane	0.24	20.46
92 n-butane	0.24	20.64
93 ethyl acetate	0.20	24.48
94 2,2-dimethylbutane	0.20	24.80
95 n-butyl acetate	0.20	24.95
96 neopentane	0.19	25.80
97 methyl-t-butylether	0.19	26.09
98 methanol	0.19	26.88
99 propane	0.17	29.73
100 n-heptane	0.17	29.91
101 acetic acid	0.14	35.08
102 t-butanol	0.14	36.36
103 propanoic acid	0.13	39.00
104 n-octane	0.12	42.07
105 acetone	0.11	45.43
106 ethane	0.11	46.47
107 n-nonane	0.09	56.34
108 acetylene	0.09	57.78
109 methyl acetate	0.08	63.25
110 t-butyl acetate	0.07	67.93
111 n-decane	0.07	68.50
112 chloroform	0.07	73.83
113 n-undecane	0.06	77.54
114 n-dodecane	0.06	88.34
115 formic acid	0.06	88.50

116 methyl chloroform	0.05	100.91
117 methyl chloride	0.04	111.30
118 tetrachloroethylene	0.04	142.15
119 methylene dichloride	0.03	148.35

5. POTENTIAL APPLICATIONS WITHIN THE ENVIRONMENT AGENCY

In this study, two equivalent methods for estimating the impact of each individual VOC species on ozone production have been proposed. The excess ozone production in ppb integrated over the downwind environment for a 1 tonne hour⁻¹ industrial emission source is the integrated downwind ozone production (IDOP). This ozone production could also be expressed as an ozone-equivalent emission ceiling, or OEC, for each emitted VOC species in tonne hour⁻¹ which when exceeded would lead to ozone concentrations in the downwind environment, which were 5 ppb higher than in the absence of that industrial VOC source. Issues associated with the use of the new method are addressed through a series of frequently asked questions and answers.

Question: How do these results relate to previously assessments of hydrocarbons using photochemical ozone creations potentials (POCPs)?

Answer: These new results have been derived using an identical photochemical trajectory model, identical detailed chemical mechanism (Master Chemical Mechanism v1.0) and identical European emission scenarios as previously used to calculate the photochemical ozone creation potentials (POCPs). Hence they are based on the same assumptions and data, and they carry the same information about atmospheric chemistry and chemical reactivity. However the new results present this information in a different context.

Both the IDOP and the POCP of a particular VOC, are examples of response functions showing the change in ozone (or relative change in the case of POCP) to a change in VOC emission under fixed, but representative meteorological conditions. To derive the POCP one considers a relative change in ozone to a change in emissions of each VOC, in turn, integrated over the entire trajectory path, in order to obtain the change in ozone production for each VOC compared with the change in ozone production for ethylene (ethene).

The POCP would describe the relative importance of the emissions of each VOC species on a mass emitted basis, each expressed as an equivalent emission of ethylene. Both POCP and IDOPs are dependent on assumptions, such as boundary conditions, under which the calculation is made. The integrated downwind ozone production, IDOP, enables one to compare two VOC species, or two emission sources, in terms of how much ozone is produced in the downwind environment under ideal conditions. This moves the concept from one of general chemical reactivity to environmental effects, and the application from one of relative importance to specific industrial process regulation.

Question: How is it envisaged that the Environment Agency could apply these new results on a sector-by-sector basis?

Answer: The method by which the Environment Agency could apply these results on a sector-by-sector basis is illustrated in Table 5.1 below. In the first example, we show how these results could be applied at the national scale.

Table 5.1 illustrates how the integrated downwind ozone production approach can be applied to the assessment of the environmental impact of two industrial processes carried out on the national scale. The first is metal surface cleaning, using organic solvents such as white spirits or kerosene, and the second is metal surface cleaning, using halocarbon solvents such as paint stripper, or dry-cleaning fluids. The UK national total emissions of each VOC species are shown in the table using the respective entries in the UK National Atmospheric Emissions Inventory and converted into the units of tonnes hour⁻¹. The next set of columns show the maximum IDOPs from Table 4.1. The final set of columns for each emission source category show the product of the emissions in tonne hour⁻¹ multiplied by the IDOPs in ppb per tonne hour⁻¹ and these are excess ozone concentrations in ppb.

The analysis in Table 5.1 shows that on a **national basis**, surface cleaning using organic solvents gives rise to a significantly smaller mass emission of VOCs compared with surface cleaning using halocarbons, but this emission has a significantly greater propensity to form ozone in the downwind environment. If all the UK emissions could be collected together and emitted from this one imaginary industrial plant, then this emission source would generate an excess of ozone of about 1.1 ppb for organic solvents and 0.7 ppb for halocarbon solvents. This would allow the conclusion to be drawn that these two emission source categories have different propensities to form ozone. The key ozone-producing species in the halocarbon solvent source category is trichloroethylene and in the organic solvent category are the aromatic compounds: 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene and propylbenzene.

Table 5.1. Application of the Integrated Downwind Ozone Production approach to the assessment of the environmental impact of two metal surface cleaning processes.

VOC species	Surface cleaning – organic solvents		Surface cleaning – halocarbon solvents			
	Emission tonne /h	IDOP ppb per tonne/h	Excess ozone (ppb)	Emission tonne /h	IDOP ppb per tonne/h	Excess ozone (ppb)
1,2,4-trimethylbenzene	0.050	4.82	0.241			
2-butanone	0.116	1.76	0.204			
n-propanol	0.116	1.42	0.165			
1,3,5-trimethylbenzene	0.024	5.09	0.123			

1,2,3-trimethylbenzene	0.022	4.68	0.102		
propylbenzene	0.016	4.17	0.066		
o-xylene	0.010	4.47	0.043		
isopropylbenzene	0.007	3.67	0.026		
m-xylene	0.004	5.52	0.020		
ethylbenzene	0.004	4.26	0.017		
p-xylene	0.003	5.00	0.017		
acetone	0.116	0.11	0.013		
decane	0.175	0.07	0.012		
n-nonane	0.101	0.09	0.009		
n-undecane	0.091	0.06	0.005		
toluene	0.001	4.10	0.005		
n-octane	0.007	0.12	0.001		
heptane	0.000	0.17	0.000		
trichloroethylene				2.134	0.27
1,1,1-trichloroethane				1.299	0.05
tetrachloroethylene				0.186	0.04
dichloromethane				0.093	0.03
Total	0.863		1.068	3.712	0.651

The question is then whether these two sectors should be given the same percentage reduction targets in terms of mass emissions. Would a strategy which focused on individual VOC species be more cost-effective?

Question: How is it envisaged that the Environment Agency could apply these new results on a site-by-site basis?

Answer: In the second example below, Table 5.2 shows how these results could be applied on a site-by-site basis.

Table 5.2 illustrates how the integrated downwind ozone production approach can be applied to the assessment of the environmental impact of several processes being operated simultaneously at a single large industrial complex. The Agency's Pollution Inventory suggests that at major industrial sites the average emission of total VOCs is between about 0.1 and 1 t/h (see Appendix A). The emission rates used in the calculations in this report are therefore comparable with likely total VOC emissions from major plant. Individual VOC species from major industrial plant may be much smaller than the values used in the calculations. It would be difficult to define a typical representative emission scenario because of local variations (see Appendix A). Illustrative emissions are used to make the necessary assessment, see Table 5.2. It is

assumed that at the large industrial complex in question, four separate processes are operating: (1) oil refining, (2) bulk organic chemicals manufacture, (3) LPG production and (4) C₄ olefin manufacture.

Table 5.2. Application of the Integrated Downwind Ozone production approach to the assessment of the environmental impact of four processes operating at a large industrial complex. Emissions quoted are illustrative only.

VOC species	Emission tonne hr ⁻¹	IDOP, ppb per tonne hr ⁻¹	Excess ozone, ppb
Oil refining			
acetylene	0.1	0.09	0.01
benzene	0.1	0.27	0.03
toluene	0.1	4.10	0.41
Total	0.3		0.45

The Agency's Pollution Inventory contains a typical profile of VOC speciation for an oil refinery with greater weighting on alkanes, propane, hexane and pentane. However the simple profile assumed here is adequate for demonstrating the approach.

Bulk organic chemicals manufacture

ethylene	0.1	8.78	0.88
propylene	0.1	4.90	0.49
styrene	0.1	2.70	0.27
Total	0.3		1.64

Liquid petroleum gas production

ethane	0.1	0.11	0.01
propane	0.1	0.17	0.02
n-butane	0.1	0.24	0.02
Total	0.3		0.05

These components are the three main contributors to the typical profile of VOC emissions from gasification processes in the Agency's Pollution Inventory.

C₄ olefin plant

butylene	0.1	8.28	0.83
1,3-butadiene	0.1	5.21	0.52
cis but-2-ene	0.1	4.84	0.48
Total	0.3		1.83

C₄ olefin is a byproduct of refining. C₄ olefin mixtures are processed to produce butadiene, butylene etc, as building blocks for other products, such as synthetic rubber, resins etc. The process shown here is taken to represent the typical manufacturing stage at a refinery.

Hence on the basis of the illustrative emission figures in Table 5.2, it could be concluded that the four processes operated at the single large industrial complex each have a significantly different impact on downwind ozone. The application to real process emissions would allow an assessment of the most important processes and individual VOCs. These important processes and VOC species could be targetted with control actions as an alternative strategy to an across-the-board emission reduction, to test cost-effectiveness.

Question: Does it matter if the same national emission total is widely distributed in a large number of small sources or rather concentrated in a few highly localised large sources?

Answer: The Integrated Downwind Ozone Production and the Ozone Equivalent Ceiling values have been calculated under scenario conditions that are designed for the national assessment context. They are likely to be more robust for the case of a large number of small sources rather than for the few highly localised sources. They were initially estimated with a view to giving advice to the Environment Agency on the magnitude of single source emissions that would generate such a small footprint on the downwind environment as to be of little practical significance.

The main difficulty with the estimation of the ozone footprint of a large isolated VOC source is that special local factors may intervene. A large industrial VOC source may be located in a coastal environment, where land-sea breezes would exert an important local influence on chemical development in the downwind environment. A large single source may be situated next to another large industrial complex emitting NO_x or chlorine, which could potentially influence chemical development in an important manner. There may be other special features in the downwind environment which would warrant attention, such as sensitive environmental areas, items of cultural heritage or population centres. Finally, individual VOCs exhibit different extents of curvature and non-linearity, which could require further detailed treatment in the case of VOC substitution in the case of a large single industrial source.

Question: Are there particular, crucial problems about evaluating mixtures?

Answer: We have tried to cover the problems involved with the evaluation of mixtures, as it was realised from the outset that VOC species are unlikely to be emitted in large quantities as pure compounds. The chemical mechanism handles accurately all of the interactions between all of the possible reaction products in a consistent manner, at least to the extent that such reactions have been identified in laboratory studies. The sensitivity analyses show that the most important interactions within pairs of species lead, generally, to a diminution of ozone production rather than to its exacerbation.

The main problem envisaged in terms of assessing the impact of mixtures is that of determining the VOC emissions and their species profiles. Once a complete and accurate breakdown of emissions by VOC species is available, the results described here should be reasonably robust and illustrative.

Question: What are the circumstances which would determine whether the Environment Agency needs to regulate individual VOC species on a site-by-site basis and when can an industry sector form the basis of control?

Answer: It is suggested that the Environment Agency apply the approach initially on a sector-by-sector approach to provide an initial screening. This would identify certain important VOC species and certain important emission source categories, or sectors, or processes. Each of the identified sectors could then be studied on a site-by-site basis to see whether the differences between individual sites are of significance.

Question: Are the complexities just too great and would a simple, but arbitrary across-the-board control strategy be preferable?

Answer: Simple strategies abound and are not difficult to formulate. The Environment Agency could ask for particular technological control solutions to be implemented, or it could prescribe percentage reductions in emissions, leaving operators to choose between the various options. Such simple strategies would always be more understandable and transparent.

The sole disadvantage with such simple strategies is that they tell you nothing about the likely environmental improvement except for the reduction in emissions. They do not require an assessment of the impact on the downwind environment, so nothing is learnt about environmental benefits. It is not therefore possible to perform an adequate analysis of costs and benefits.

Increasingly, policy-makers are being asked to consider effects-based approaches. The concept of integrated downwind ozone production and ozone-equivalent emission ceiling are a first step towards defining how impacts in the downwind environment might be quantified for VOC emissions.

Question: How might these results be followed up, improved or extended with further research?

Answer: The IDOP approach offers a substantial advance on the POCP approach because the focus moves from one of emission equivalence to ozone production in the downwind environment. Over the period since the development of the IDOP and POCP approaches, the underlying chemistry has improved significantly and advantage should be taken of the development of MCMv3.0 to recalculate the IDOPs.

6 CONCLUSIONS

Ranking VOCs according to their maximum integrated downwind ozone production (Table 4.1) is useful, its interpretation is open to some debate. Should the numbers be treated in absolute terms, or relative terms, or just qualitatively, since rather different absolute amounts of ozone can be generated according to the detailed conditions assumed? This study has made no attempt to group the VOCs and thereby simplify Table 4.1 further, using a smaller number of VOC categories. This may be necessary when detailed information on the emissions of each VOC species is not available. Can this grouping be made more rigorous?. Two methods come to mind: data mining and using the VOC to NO_x ratio. Ways of attempting to categorise the results presented in this study, using data mining, are given in another report (Jensen, Waldron and Fisher 2003). Results are inconclusive suggesting that the full description of the chemistry of

each VOC is required for an impact assessment. However the studies completed rely on a number of detailed assumptions regarding the model and it has not been demonstrated that the results are insensitive to all possible changes to these assumptions. A precautionary approach has been taken, which lessens concerns about these assumptions, but further work is needed to see how the method would work in practice.

The next step could be to evaluate, on a national basis, all of the VOC-emitting sectors under Environment Agency control, using the VOC species profiles compiled within the National Atmospheric Emissions Inventory, NAEI or the Environment Agency's Pollution Inventory. This would link information on VOC species handled by the Master Chemical Mechanism MCM and the speciation profiles held within the NAEI and Pollution Inventory, for each sector. The sectors could then be ranked in order of their integrated downwind ozone production and their mass emission rates, and the same could be done for the individual VOC species.

Following this, the next step could then be to evaluate, on a site-by-site basis, each of the main VOC-emitting industrial complexes using emissions data held by the Environment Agency. The issue would again be to link the species, known to be emitted at each site, and the VOC species carried by the Master Chemical Mechanism. The processes could then be ranked in order of their significance for ozone formation in the downwind environment, and the same could be done for individual VOC species. Typical emission rates of VOCs from industrial sectors and individual processes are given in Appendix A. These illustrate that conditions considered in this study are relevant to real processes, with a tendency to consider emissions larger than normally expected. This suggests further investigation to check that the assessed impact is not too precautionary.

Steps could also be taken using the Pollution Inventory to extend the Master Chemical Mechanism to an evaluation of the IDOPs and EOCs for all the VOC species currently reported. These species could then be added to the various VOC profiles, to complete an assessment of the likely impacts of the Environment Agency regulated plant on ozone in the British Isles. The results should allow an examination of the likely impacts of the VOC emission reductions proposed as part of the UN ECE Gothenburg Protocol and the EU National Emission Ceilings Directive.

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APPENDIX A. BRIEF OVERVIEW OF VOC EMISSIONS FROM INDUSTRIAL PROCESSES

Emissions of VOCs from Agency regulated processes can be obtained from the Pollution Inventory. Figure A1 shows that the majority of emissions are derived from the chemical industry sector (84%), which is made up of organic chemical processes (39%), petrochemical process (29%) and halogens (15%). The fuel and power supply sector accounts for 10% of emissions.

Table A1 lists the sites with the highest emissions of VOCs as provided by the Agency's website. The majority of these sites are classed in the Fuel and Power Production sector or the Chemical Industry sector. The fifteen sites with the highest emissions contribute approximately two thirds of the total emissions.

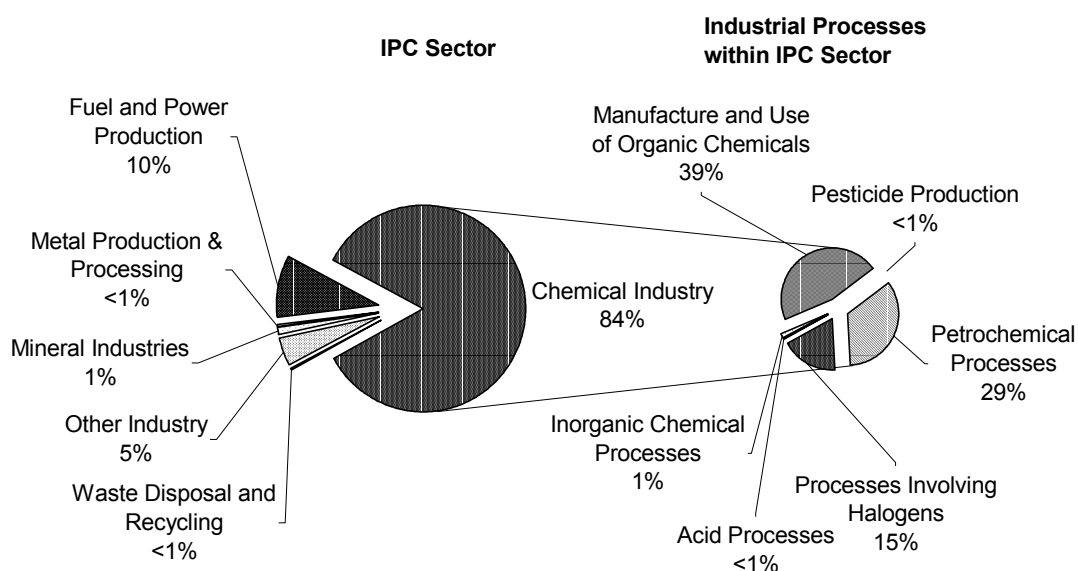


Figure A1 Agency-Regulated Sources of VOCs: 1998

Table A1 Sites with the largest releases of total VOCs to air: 1998

Company Name	Location	Industry Sector	Amount tonnes	% of Agency releases
BP Oil (UK) Ltd	Coryton Refinery, Stanford-Le-Hope, Essex	Fuel and Power Production and Associated Processes	13,500	10.7%
Shell (UK) Ltd	Stanlow, Cheshire	Fuel and Power Production and Associated Processes	5,900	7.4%
Conoco Ltd	Humber Refinery, Immingham	The Chemical Industry	3,360	
		Fuel and Power Production and Associated Processes	7,700	6.1%
The Associated Ocel Co Ltd	Cheshire	The Chemical Industry	6,990	5.6%
		Metal Production and Processing	26.4	
BASF Plc	Seal Sands, Middlesbrough	The Chemical Industry	6,720	5.3%
Lindsey Oil Refinery Ltd	Killingholme, Immingham	Fuel and Power Production and Associated Processes	6,500	5.2%
Dupont (UK) Ltd	Wilton, Teesside	The Chemical Industry	4,840	3.8%
Texaco Ltd	Pembroke Plant, S. Wales	Fuel and Power Production and Associated Processes	4,800	3.8%
BP Chemicals Ltd	Saltend, Hull	The Chemical Industry	4,310	3.4%
Elf Oil UK Ltd	Milford Haven Refinery, S. Wales	Fuel and Power Production and Associated Processes	3,530	2.8%
Conoco Ltd	Theedlethorpe St. Helen	Fuel and Power Production and Associated Processes	3,200	2.5%
Shell UK Ltd	Stanford-Le-Hope, Essex (now closed)	Fuel and Power Production and Associated Processes	3,170	2.5%
Philips Petroleum Co (UK) Ltd	Seal Sands, Middlesbrough	Fuel and Power Production and Associated Processes	2,930	2.3%
Glaxo Wellcome Operations	Ulverston, Cumbria	The Chemical Industry	1,250	2.1%
ICI Chemicals and Polymers	Wilton, Teesside	The Chemical Industry	2,000	1.6%

APPENDIX B. PROPORTION OF EMISSIONS OF VOCs FROM INDUSTRIAL SOURCES IN URBAN AREAS

It is also important to compare the importance of industrial VOC emissions with those from other sources. This can be derived from the Pollution Inventory. Greater Manchester emits the highest mass of industrial VOCs (approximately 105 kt/a) - nearly twice that of the second largest emitter, London (approximately 60 kt/a). However, the highest annual density of industrial emissions is in Middlesborough (approximately 136 t/km²). These are illustrated in Figure A2.

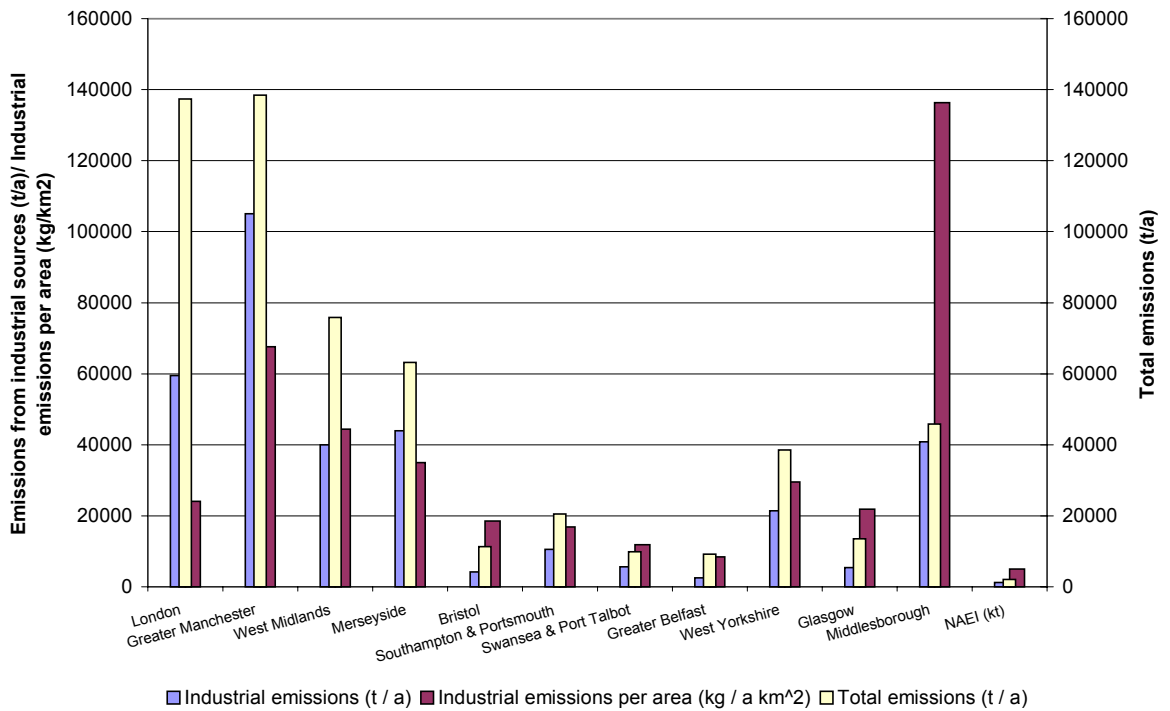


Figure A2 Mass and density of VOC emissions in urban areas