

**MEASUREMENTS OF PEROXY RADICALS
IN THE MARINE BOUNDARY LAYER**

Thesis submitted for the degree of
Doctor of Philosophy
at the University of Leicester

by

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Measurements of Peroxy Radicals in the Marine Boundary Layer

by Gavin Salisbury, April 2001

Abstract

This thesis focuses on measurements of peroxy radicals, which are reactive intermediates in the oxidation of organic species in the troposphere. Laboratory experiments with a Peroxy Radical Chemical Amplification (PERCA) instrument have shown that the chain length (CLN) of the inlet amplification reaction decreases markedly with increasing specific humidity. The magnitude of the effect is reduced by warming the inlet to above ambient temperatures. Modelling of the PERCA inlet chemistry using the measured CLN(wet)/CLN(dry) ratios for given temperature and humidity gave fitted hydroperoxy radical (HO_2) wall-loss rate coefficients in good agreement with literature measurements, which would suggest that enhanced wall losses of HO_2 in humid air are sufficient to explain the observed CLN-humidity effect.

A study of night-time chemistry at Mace Head in Ireland during the Eastern Atlantic Spring Experiment, 1997 (EASE 97) has shown that the oxidation of alkenes at night by reaction with ozone was greater by a factor of four than that by reaction with the nitrate radical, NO_3 , over the whole EASE 97 data set. The sustained mixing ratios of peroxy radicals observed at night demonstrated a requirement for substantial radical production processes, in the absence of daytime photochemistry. Peroxy radical rate of production analyses showed that ozone reactions produced more peroxy radicals over the whole night-time period (defined as where $[\text{NO}_3] \neq 0$) than nitrate reactions (66 *versus* 34%, on average). However, the two mechanisms were found to operate at a similar rate in the middle of the night, when $[\text{NO}_3]$ was highest.

Analysis of photochemical ozone tendency by wind sector during the Eastern Atlantic Summer Experiment, 1996 (EASE 96) and Spring Experiment, EASE 97 has shown that net photochemical ozone production at Mace Head was dominated by polluted air masses originating in Britain and continental Europe for both summer 1996 and spring 1997 (southeasterly wind sector). The proportion of such polluted air masses encountered at Mace Head was much greater in the spring than in the summer; in addition, the ozone tendency was greater for each wind sector in the spring campaign than in the summer campaign. These two factors combined to ensure that the average ozone production rate was two times higher for spring 1997 than for summer 1996: $0.5^{+0.3}_{-0.2}$ ppbv h^{-1} for EASE 96, $1.0^{+0.5}_{-0.3}$ ppbv h^{-1} for EASE 97. The error limits allow for the likely magnitude of the humidity effect on the PERCA measurements. In contrast, ozone tendency calculations for the Southern Ocean Atmospheric Photochemistry Experiment 2 (SOAPEX 2), held at Cape Grim, Tasmania, in Austral summer 1999, have shown that daytime ozone production and destruction were finely balanced for much of the campaign; little difference was observed between clean-air (baseline) and 'semi-polluted' (non-baseline) conditions.

The laboratory CLN-humidity measurements have been used to compare the peroxy radical mixing ratios observed during several field campaigns with both a low- NO_x steady-state expression for the sum of peroxy radicals, $[\text{HO}_2 + \text{RO}_2]$, and the $[\text{HO}_2 + \text{RO}_2]$ output from two box-modelling studies of the EASE campaigns, with mixed success. The steady-state expression compared best with the humidity-corrected baseline peroxy radical mixing ratios from the SOAPEX 1 campaigns, held at Cape Grim in 1995. In the model *versus* measurement comparisons, there was no clear relationship between model/measurement ratio and the nature of the air mass. In some cases, the modelled/measured $[\text{HO}_2 + \text{RO}_2]$ ratio was closer to one than expected, based on the calculated magnitude of the PERCA CLN-humidity effect.

Acknowledgements

I would like to thank Paul and the other members of the PSM group – Gavin E., Gavin P., Andrew, Gary and Mona, for their help and encouragement. In particular, thanks to Dr Edwards for his help in setting up the PERCA when I first arrived, to Gav. P. for keeping me on the *way of the flat-pack* for the second half of this project, and to Andrew for his relentless sociability. Thanks also to Tim Green, Graham Mills and Lucy Carpenter for help during SOAPEX, Keith, John W., Phil and Gerry B. for their logistical support of this project, Prodromos Zanis for help with the early humidity experiments, and thanks to the NERC for funding.

Many thanks also to Vickie Owen, for missing me when I didn't turn up. Finally, I owe a huge debt of gratitude to Dr Smith at the University of Reading and everyone at Eldon Day for sticking with me and helping me to reach this point, and to all members of the Winterbourne T.C. during my sojourn there for people and times to carry with me always.

The Nazca lines

We copy the world in miniature,
line up model valleys
to model mountains:

we must attract our gods'
attention – make them see
our need and cry.

*

We cover the lines
every day, massage the land
that the mountainous tears
might fill our channels.

We take our turns,
sing the songs
but it makes no difference:

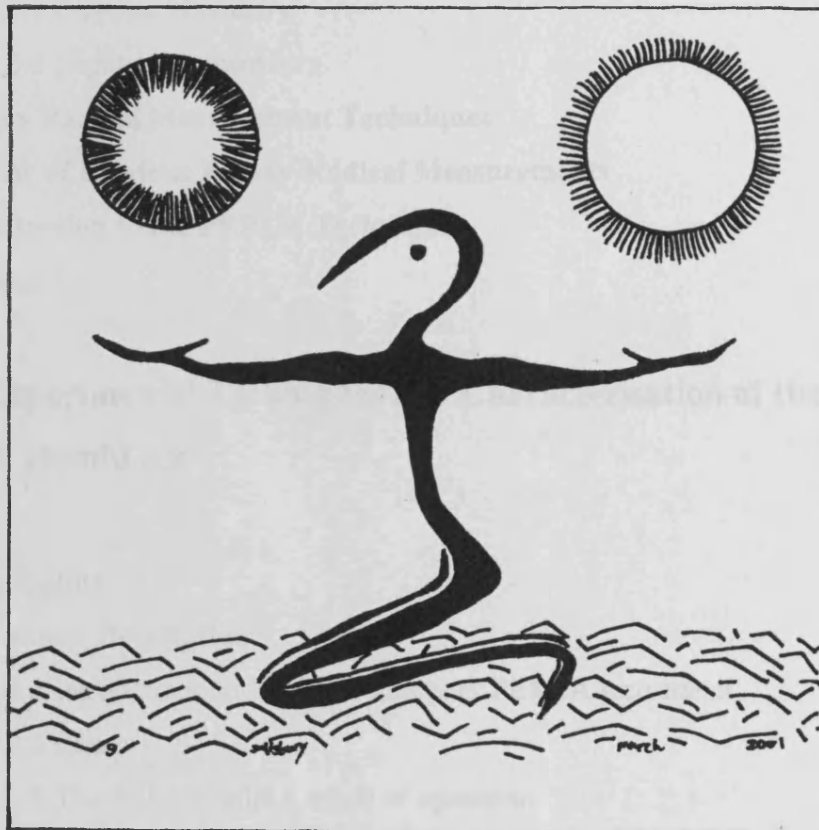
our lines must be misaligned,
our models somehow false

so we build more.
We scar the land to stay alive.

There must be a place

Home is too far
gone, and we can't remember now
how we were born.

The whole way back
is out of



reach. Yet
there must be a place

somewhere between:
closer to here and there,
where we can be safe and live.

Leicester, 20th September 2000

Contents

Chapter 1 - Introduction	1
1.1 The Earth's Atmosphere	1
1.2 The Troposphere	1
1.3 Introduction to Tropospheric Chemistry	2
1.3.1 Daytime chemistry	2
1.3.2 Night-time chemistry	5
1.4 Peroxy Radical Measurement Techniques	5
1.5 Review of Previous Peroxy-Radical Measurements	6
1.6 Introduction to the PERCA Technique	12
1.7 Summary	13
 Chapter 2 - Experimental Techniques and Characterisation of the PERCA Instrument in Humid Air	 14
2.1 Introduction	14
2.2 Instrument Description	15
2.2.1 Introduction to the UEA-Leicester PERCA instrument	15
2.2.2 Gases	16
2.2.3 The PERCA inlet – mode of operation	17
2.2.4 Chain length optimisation	20
2.2.5 Data acquisition	22
2.3 NO₂ Calibrations	22
2.4 Peroxy Radical Calibrations	24
2.4.1 Calibration method	24
2.4.2 Photolysis cell wall-loss experiments	25
2.4.3 $j(\text{CH}_3\text{I})$ determinations	27
2.4.4 Cross-calibration with the University of East Anglia aircraft PERCA instrument, 28 th -30 th June 1999	29

2.4.5 Cross-calibration with the University of Leeds FAGE HO ₂ source, 21 st -22 nd September 1998	30
2.5 Discussion of Uncertainties in the PERCA Measurements	33
2.6 Variation of the PERCA chain length with temperature and humidity	35
2.6.1 Introduction to the temperature/humidity characterisation experiments	35
2.6.2 Dependence of the PERCA chain length on temperature in dry air	36
2.6.3 Humidity experimental details	38
2.6.4 Dependence of the PERCA chain length on humidity	39
2.6.5 Dependence of the PERCA chain length on humidity and temperature	40
2.6.6 Modelling of the PERCA inlet chemistry	42
2.7 Summary	47
2.7.1 General summary	47
2.7.2 PERCA Instrument Characterisation in Humid Air	48
 Chapter 3 – Night-time Chemistry at Mace Head, Ireland	 50
 3.1 Introduction	 50
3.2 The EASE 97 Campaign	55
3.2.1 Measurement site	55
3.2.2 Other measurements	55
3.2.3 Data analysis	56
3.3 The Nitrate Radical during EASE 97	58
3.4 Peroxy Radicals at Night during EASE 97	63
3.4.1 Introduction	63
3.4.2 Results	63
3.4.3 Comparison with University of Leeds FAGE HO ₂ and OH measurements	69
3.5 Peroxy Radical Production at Night during EASE 97	71
3.6 Summary and Conclusions	83

Chapter 4 – A Seasonal Comparison of Ozone Photochemistry at Mace Head, Ireland

86

4.1 Introduction	86
4.1.1 Ozone photochemistry in the troposphere	86
4.1.2 Measurements during EASE 96 and EASE 97	87
4.2 Data Analysis – Air Mass Classifications	87
4.2.1 Data classification method	87
4.2.2 Comparison of the wind sector analysis with other data classification methods	89
4.3 Chemical Climatologies for EASE 96 and EASE 97 by Wind Sector	98
4.4 The PERCA Measurements during EASE 96 and EASE 97	103
4.4.1 Introduction	103
4.4.2 Comparison of peroxy radical mixing ratios during EASE 96 and EASE 97	103
4.5 Photochemical Ozone Tendencies during the EASE Campaigns	109
4.5.1 Day-by-day analysis	109
4.5.2 Wind sector comparison	117
4.6 Ozone Compensation Point	123
4.7 Ozone Production Efficiency	126
4.7.1 Calculation of ozone production efficiency	126
4.7.2 Ozone production efficiency and ozone tendency	128
4.8 Summary and Conclusions	129

Chapter 5 – The SOAPEX 2 Experiment: Cape Grim, January-February 1999

133

5.1 Introduction	133
5.1.1 Background to the SOAPEX campaigns	133
5.1.2 Measurement site	134
5.1.3 Comparison of SOAPEX 1a and 1b	134
5.1.4 PERCA underestimation of peroxy radical mixing ratios during SOAPEX 1	138
5.2 The SOAPEX 2 Campaign	139

5.2.1 Objectives of the experiment	139
5.2.2 Measurements and instrument operators during SOAPEX 2	140
5.3 The PERCA Measurements during SOAPEX 2	140
5.3.1 Instrument operation	140
5.3.2 Correlations of $[\text{HO}_2 + \text{RO}_2]$ with $j(\text{O}^1\text{D})$	142
5.3.3 Calculation of k' from peroxy radical data	145
5.3.4 Comparison of measured peroxy radicals with levels calculated from peroxide data	146
5.3.5 Comparison of FAGE and PERCA peroxy radical measurements during SOAPEX 2	148
5.4 Classification of Air Masses during SOAPEX 2	150
5.4.1 Introduction to the classification methods	150
5.4.2 Results of the air mass classifications	152
5.4.3 Air mass classification summary and conclusions	156
5.4.4 Comparison of pollution tracer levels between SOAPEX 1a, SOAPEX 2 and the EASE campaigns	157
5.5 Ozone Photochemistry during SOAPEX 2	158
5.5.1 Ozone tendencies	158
5.5.2 Peroxide production and ozone tendency	161
5.5.3 Ozone compensation point	162
5.5.4 Ozone production efficiency	164
5.6 SOAPEX 2 Daytime HO_x Sources and Sinks	166
5.6.1 Daytime HO_x sources other than ozone photolysis	166
5.6.2 HO_x sources: comparison with EASE 97	169
5.6.3 OH loss reactions during SOAPEX 2	170
5.7 The NO_x Balance During SOAPEX 2: Comparison with EASE 97	171
5.8 SOAPEX 2 Night-time Chemistry	173
5.8.1 Introduction	173
5.8.2 Baseline and non-baseline night-time chemistry	174
5.8.3 Peroxy radical production at night	175
5.8.4 Daytime and night-time comparison	175
5.8.5 Comparison with EASE 97	177
5.9 Summary	177

Chapter 6 – Towards a Humidity Correction for the PERCA Instrument	181
6.1 Introduction	181
6.2 Calculated CLN-Humidity Effect for EASE 96, EASE 97 and SOAPEX 2	181
6.2.1 PERCA inlet temperature and ambient humidity during EASE 96, EASE 97 and SOAPEX 2	181
6.2.2 Calculation of expected CLN reduction in humid air for each campaign	183
6.3 Comparison of Measured and Calculated ‘Clean-Air’ Peroxy Radical Mixing Ratios	184
6.4 Comparison of Measured Peroxy Radicals during EASE 96 and EASE 97 with Box Model Results	187
6.4.1 Comparison method	187
6.4.2 The University of Leeds generic box model	188
6.4.3 Results of the Leeds-model/measurement comparison	189
6.4.4 The University of East Anglia (UEA) modelling study of radical chemistry during EASE 96	191
6.4.5 Discussion of the model/measurement comparisons	192
6.5 Summary and Conclusions	193
 Chapter 7 – Conclusions and Suggestions for Further Research	 195
7.1 Conclusions	195
7.1.1 Introduction	195
7.1.2 Characterisation of the PERCA instrument in humid air	195
7.1.3 Ozone photochemistry at Mace Head and Cape Grim	197
7.1.4 Night-time chemistry at Mace Head and Cape Grim	199
7.2 Suggestions for Further Research	200
7.2.1 Laboratory work	200
7.2.2 Humidity correction	200
7.2.3 Field campaigns	200

Appendix – Calculation of specific humidity from relative humidity and temperature	201
Publications	203
Postgraduate Record	204
References	209

Chapter 1 - Introduction

1.1 The Earth's Atmosphere

The Earth's atmosphere consists largely, over 99% by volume, of nitrogen, oxygen, argon and variable amounts of water vapour. The remaining 1% is made up of so-called *trace* gases. These trace species can arise from natural sources, such as volcanism and biological processes, or they can be anthropogenic in origin. A great deal of research effort has been spent in recent years in examining humanity's influence on atmospheric composition, since the trace compounds and their relationships with one another are vital to the survival of all living organisms.

Much of the chemistry which occurs in the atmosphere is driven by sunlight. This is as true of the human-induced phenomena of the industrial age, such as the Antarctic ozone hole in the stratosphere, acid rain and photochemical smog, as it is of the natural processing which previously kept atmospheric composition relatively stable over very long timescales. An important aim of this project is to examine in detail aspects of atmospheric photochemistry occurring in unpolluted conditions near the Earth's surface in order to understand more fully what happens when those conditions are perturbed by human activity.

1.2 The Troposphere

The work presented in this thesis relates to the lowest region of the atmosphere, known as the *troposphere*. The troposphere is divided into two distinct regions, the surface *boundary layer* and the overlying *free troposphere*. The boundary layer extends from the Earth's surface up to a height of between 0.5 and 2 km during the day and is characterised by highly turbulent mixing. The free troposphere extends from the top of the boundary layer up to a height of *ca* 10 km, known as the *tropopause*, where the stratosphere begins. The boundary layer is crucial to overall atmospheric composition, since it is at the surface that the bulk of pollutants, as well as natural trace species, are emitted. *Stull* [1988] showed that the boundary layer responds to surface effects such as frictional drag, heat transfer and pollutant emissions very quickly, on a timescale of *ca* 1 h. The present project is concerned only with measurements made close to the Earth's surface, *i.e.*, entirely within the planetary boundary layer.

1.3 Introduction to Tropospheric Chemistry

1.3.1 Daytime chemistry

The fate of a molecule emitted at the Earth's surface depends on its lifetime with respect to photolysis and/or oxidation, although physical processes, such as deposition, must also be considered for many species. The primary daytime oxidant in the troposphere is the hydroxyl (OH) radical, formed by the photolysis of ozone, followed by reaction of the resultant excited oxygen atom with water:



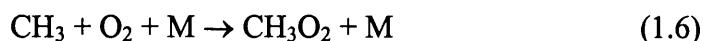
$$(\lambda < 340 \text{ nm})$$



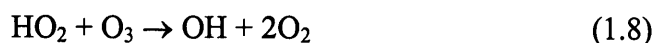
OH reacts at significant rates with most atmospheric pollutants, leading to their removal over a range of timescales. In the relatively clean atmosphere, where NO_x ($\text{NO} + \text{NO}_2$) and non-methane hydrocarbon (NMHC) levels are low, the main sinks for the OH radical are its reactions with carbon monoxide (CO) and methane (CH_4):



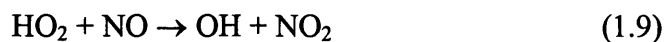
The H atom and CH_3 radical subsequently react rapidly with oxygen to form the hydroperoxy and methylperoxy radicals (HO_2 and CH_3O_2), respectively:



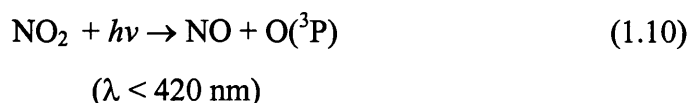
where M represents a nitrogen or oxygen molecule. Other peroxy radicals (RO_2) are formed analogously in the course of the oxidation of a wide range of organic species by OH. Under low- NO_x conditions the oxidation of CO leads to further ozone destruction *via* reactions (1.7) and (1.8):



although the major loss processes for the peroxy radicals are their self- and cross-reactions to form peroxides (see also Chapters 4 and 5). Under more polluted conditions, where significant mixing ratios of NO are present, reaction with NO represents an important loss process for the peroxy radicals, and at the same time produces NO₂:



Photolysis of NO₂ (with rate coefficient $j(\text{NO}_2)$) then leads to ozone production *via* reactions (1.9) and (1.10):



Ozone production *via* the oxidation of NO to NO₂ by peroxy radicals in moderately polluted air represents a perturbation of the *photochemical steady state* (PSS) of ozone in the daytime troposphere, which is applicable when there are no local sources of NO_x and the actinic flux is relatively constant. The PSS is an ozone null cycle consisting of reactions (1.10-1.12):



and is often expressed as a ratio:

$$\phi = \frac{j(\text{NO}_2)[\text{NO}_2]}{k_{12}[\text{NO}][\text{O}_3]} \quad (1.13)$$

In the absence of any species other than ozone which oxidises NO to NO₂, the value of the ratio ϕ is one; where sufficient peroxy radicals are present, ϕ may be significantly greater than one. This perturbation of the ozone PSS has been used to estimate peroxy radical mixing ratios under polluted conditions [*e.g.*, Cantrell *et al.*, 1993b; Carpenter *et al.*, 1998].

It may readily be seen that measurements of peroxy radical mixing ratios can give useful information on the tropospheric photochemical ozone budget, since peroxy radicals are intimately involved in both the production and destruction of tropospheric ozone. Indeed,

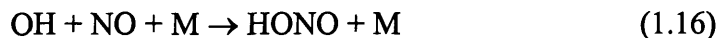
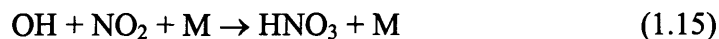
knowledge of peroxy radical levels in a given air mass allows calculation of the net *in-situ* rate of ozone production or destruction, or *ozone tendency*, $N(O_3)$:

$$N(O_3) = k_P[NO][HO_2+RO_2] - \{fj(O^1D) + k_7[OH] + k_8[HO_2]\}[O_3] \quad (1.14)$$

where k_P is a combined rate coefficient for the oxidation of NO to NO₂ by all peroxy radicals, $j(O^1D)$ is the photolysis rate coefficient of ozone to yield O(¹D) atoms (reaction 1.1), f is the proportion of O(¹D) atoms which react with water to give OH (reaction 1.2) rather than being collisionally deactivated, and k_7 and k_8 are the rate coefficients for reactions (1.7) and (1.8), respectively.[†] The NO mixing ratio required for ozone production to equal ozone destruction ($N(O_3)=0$) is often called the *ozone compensation point*, and may be estimated from $N(O_3)$ calculations. These implications of peroxy radical chemistry are discussed in detail for two different coastal sites in Chapters 4 and 5.

The photochemical production of excess ozone in the urban polluted troposphere is of major environmental concern, since it causes human health problems and has a negative impact on local agriculture and forestry. On a larger scale, the average tropospheric ozone mixing ratio in the Northern Hemisphere as a whole has approximately doubled in the last hundred years, and is still increasing [e.g., *Finlayson-Pitts and Pitts*, 2000]. In addition, an annual cycle in ozone mixing ratios has been observed at a wide variety of measurement sites in the Northern Hemisphere, with a broad maximum in spring and a minimum in summer [e.g., *Derwent et al.*, 1998; *Monks*, 2000, and references therein]. Assessment of the contribution of *in-situ* photochemical ozone production to this pattern is an important ongoing research area in atmospheric chemistry. As previously noted, ozone production in the troposphere requires both volatile organic compounds (VOCs), which are oxidised by OH to give peroxy radicals, and NO_x. Under high-NO_x conditions, usually in urban centres, ozone production is VOC-limited, whereas under the low-NO_x, ‘semi-polluted’ conditions often found in rural areas, ozone production is generally NO_x-limited [e.g., *Sillman*, 1999; *Rickard et al.*, 2001]. The *ozone production efficiency* in the NO_x-catalysed cycle represented by reactions (1.9-1.11) is often defined as the number of ozone molecules produced per molecule of NO_x lost to the cycle *via* oxidation reactions such as (1.15) and (1.16) [e.g., *Liu et al.*, 1987; *Carpenter et al.*, 2000]:

[†] Equation (1.14) neglects other ozone loss processes, in particular halogen-atom reactions; see Chapters 4 and 5 for further discussion of this point.



Ozone production efficiency represents a useful indicator of NO_x/VOC limitation, and its evaluation and use are considered in Chapters 4 and 5.

1.3.2 Night-time chemistry

At night, in the absence of sunlight, photolysis of ozone cannot occur, so that OH is generally present only at very low mixing ratios. However, peroxy radicals may be produced at night *via* alternative mechanisms involving the oxidation of organic species by ozone and the nitrate radical (NO_3); discussion of these processes is deferred until Chapter 3, where a detailed case study of night-time chemistry at Mace Head on the Atlantic coast of Ireland, during the Eastern Atlantic Spring Experiment, April-May 1997 (EASE 97), is presented.

1.4 Peroxy Radical Measurement Techniques

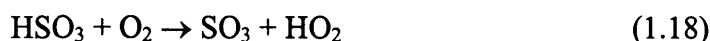
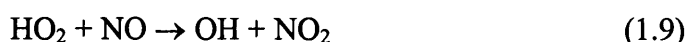
Four methods have been used for measurements of peroxy radicals in the troposphere: Matrix-Isolation Electron-Spin Resonance [MIESR; *Mihelcic et al.*, 1985, 1990, 1993]; Fluorescence Assay by Gas Expansion [FAGE; *e.g.*, *Hard et al.*, 1992; *Creasey et al.*, 1997; *Mather et al.*, 1997]; Peroxy radical Chemical Amplification [PERCA; *e.g.*, *Cantrell et al.*, 1984, 1992; *Clemmshaw et al.*, 1997], which is the technique used in this project (see Section 1.6, and Chapter 2 for experimental details), and Ion-Molecule-Reaction Mass Spectrometry [IMR-MS; *Reiner et al.*, 1997, 1999].

The MIESR technique consists in the trapping of ambient air samples in a D_2O matrix at 77 K, followed by detection of radical species by electron spin (paramagnetic) resonance. The timescale for sample collection is relatively slow (*ca* 30 min), although a variety of species can be determined from a single sample to high accuracy ($\pm 5\%$), including NO_2 , NO_3 , HO_2 , the peroxyacetyl radical ($\text{CH}_3\text{C}(\text{O})\text{O}_2$), and the sum of the alkylperoxy radicals, ΣRO_2 [*Mihelcic et al.*, 1985, 1990, 1993].

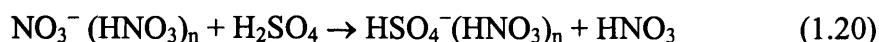
The FAGE technique is based on the on-resonance laser-induced fluorescence (LIF) detection of the hydroxyl radical (OH), generally in the $\text{A}^2\Sigma^+ (v''=0) - \text{X}^2\Pi^+ (v'=0)$ transition at *ca* 308 nm. Ambient air is pumped through a 1 mm inlet nozzle into a sample chamber held at low pressure (<1 Torr), so that the fluorescence lifetime of OH is of the order of 100-200 ns.

This procedure, in combination with very short laser pulses (<25 ns) at high repetition rates (7–10 kHz), allows the separation of the fluorescence signal from scattered laser light at the same wavelength. HO₂ is measured by adding NO to the ambient airflow, which converts HO₂ to OH with a calibrated efficiency *via* reaction (1.9), and subsequent detection of OH as previously. Measurements with a time resolution of 150 s are possible, with typical detection limits of 5×10^5 molecules cm⁻³ for OH and 2.5×10^6 molecules cm⁻³ for HO₂ [Hard *et al.*, 1992; Creasey *et al.*, 1997; Mather *et al.*, 1997; Carlsaw *et al.*, 2000a].

The IMR-MS technique is based on the amplifying chemical conversion of peroxy radicals to sulphuric acid, followed by the detection of sulphuric acid by ion-molecule-reaction mass spectrometry. The reaction sequence is as follows:



The sulphuric acid produced in reaction (1.13) is detected using the ion-molecule reaction



The detection limit of the IM-RMS technique is estimated to be $<10^7$ molecules cm⁻³, with an accuracy of *ca* $\pm 30\%$ [Reiner *et al.*, 1997, 1999]. Peroxy radical measurements made to date by each of these techniques are discussed in the next section.

1.5 Review of Previous Peroxy Radical Measurements

A summary of the peroxy radical measurements reported to date, including measurement location and some notes on major points of interest, is given in Table 1.1. Table 1.1 clearly shows that the two most important techniques thus far in the study of peroxy radicals in the real atmosphere have been the PERCA and FAGE techniques. The MIESR technique perhaps proved too cumbersome for field operation, and appears to have fallen into disuse; the IMR-MS technique is, by contrast, relatively new, and may become important in the future.

A great deal of research effort has been devoted to the development of peroxy radical measurement techniques from aircraft platforms in the last decade, and working instruments based on the PERCA [T. Green *et al.*, unpublished results], FAGE [Jaeglé *et al.*, 1997, 1998, 1999, 2000] and IMR-MS [Reiner *et al.*, 1999] techniques are all now in operation around the world. Nevertheless, the majority of published peroxy radical measurements have been made at ground stations, albeit under various atmospheric conditions. Specifically, many of the reported peroxy radical measurements have been made at mountain-top sites either in free tropospheric [Cantrell *et al.*, 1996a, 1996b; Zenker *et al.*, 1998; Zanis *et al.*, 1999, 2000a,b] or in fairly polluted [Mihelcic *et al.*, 1993] air masses. The only extensive data set of peroxy radical measurements in the clean or semi-polluted boundary-layer environment has been achieved using the FAGE and PERCA techniques within the last six years [Carpenter *et al.*, 1997; Carslaw *et al.*, 1997, 1999a, 2001a; Creasey *et al.*, 1997; Monks *et al.*, 1996, 1998, 2000; Penkett *et al.*, 1997; Savage *et al.*, 2001]. This data set includes measurements taken at Cape Grim in Tasmania [Carpenter *et al.*, 1997; Monks *et al.*, 1996, 1998, 2000; Penkett *et al.*, 1997], Mace Head in Ireland [Carslaw *et al.*, 1999a, 2001a; Monks *et al.*, 2001] and Weybourne in Norfolk, England [Carpenter *et al.*, 1997; Carslaw *et al.*, 1997b]. Most of these data were taken using two successive generations of a PERCA instrument built and developed at the University of East Anglia, the first of which was described in detail by Clemitshaw *et al.* [1997]. The modified second-generation instrument was used during the measurement campaigns presented in this thesis (see Chapter 2).

The SOAPEX 1 (Southern Ocean Atmospheric Photochemistry Experiment 1) measurement campaigns at Cape Grim in 1995 represent arguably the most extensive experimental examination of ozone photochemistry in the remote marine boundary layer yet undertaken [see particularly Penkett *et al.*, 1997]. The SOAPEX 2 campaign, which took place at the same location during January-February 1999, was designed to extend the results of the first experiment, in the sense that a much-expanded set of atmospheric trace species was measured, including a wide range of organic compounds, the nitrate radical, and the sum of oxidised nitrogen species, NO_y . Both PERCA [$\text{HO}_2 + \text{RO}_2$] and FAGE [HO_2] measurements were made during the campaign, and the PERCA measurements obtained during SOAPEX 2 are described in detail in Chapter 5.

Table 1.1 Summary of previous peroxy radical measurements

Campaign (Acronym)	Location, Year	Technique(s)	Midday max. [HO ₂] or [HO ₂ +ΣRO ₂] Observed /pptv	Comments	Reference (s)
-	Oregon, 1986-7	FAGE (HO ₂)	8	One coastal site, one urban site; similar maxima at both sites for clear-sky conditions	<i>Hard et al.</i> , 1992
-	Schauinsland, 1990	MIESR	40	Forested location; anti-correlation between RO ₂ and NO ₃ at night	<i>Mihelcic et al.</i> , 1993
ROSE 1	Alabama, 1990	PERCA	200	Forested location; measured levels compared well with PSS calculations	<i>Cantrell et al.</i> , 1992, 1993b, 1995
MLOPEX 2	Mauna Loa, 1991-2	PERCA	25	Free troposphere; upslope/downslope effects; measurements low compared with PSS calculations; peroxy radicals observed at night	<i>Cantrell et al.</i> , 1995, 1996a,b, 1997b; <i>Hauglustaine et al.</i> , 1999
SONTOS	Ontario, 1992	PERCA	23	Rural site	<i>Arias and Hastie</i> , 1996
OCTA	Izaña, Tenerife, 1993	3 PERCA instruments and 1 MIESR instrument	80-100	2 PERCA instruments within 25% of MIESR instrument, 1 systematically low	<i>Zenker et al.</i> , 1998
-	Denver, Colorado, 1993	PERCA	20-80	Urban site; reactions of O ₃ with alkenes claimed as important source of peroxy radicals at night	<i>Hu and Stedman</i> , 1995

Table 1.1 (cont.)

Campaign (Acronym)	Location, Year	Technique(s)	Midday max. [HO ₂] or [HO ₂ +ΣRO ₂] Observed /pptv	Comments	Reference (s)
FIELDVOC	Brittany, 1993	PERCA	60	Measurements much lower than PSS calcs; low night-time levels	<i>Cantrell et al.</i> , 1996c
LAFRE	Los Angeles, 1993	FAGE (HO ₂)	8	Measurements in smog; poor agreement with simple model at midday	<i>George et al.</i> , 1999
TOHPE	Idaho Hill, Colorado, 1993	FAGE(HO ₂), PERCA	6 (HO ₂), 60	RO ₂ /HO ₂ ratio 4-15 times larger than predicted; HO ₂ /OH ratio in range 15-80: agreed well with theory for [NO] > 100 pptv; factor of 3-4 too low under clean conditions	<i>Cantrell et al.</i> , 1995, 1997a; <i>Mather et al.</i> , 1997; <i>Stevens et al.</i> , 1997
PRICE I	Schauinsland, 1994	4 PERCA instruments and 1 MIESR instrument	25 (PERCA), 50 (MIESR)	No systematic difference between PERCA instruments; MIESR instrument measured systematically higher	<i>Carpenter</i> , 1996
WAO-TIGER	Weybourne, Norfolk, 1993-5	PERCA	12	Positive correlation of peroxy radicals and NO ₃ observed at night	<i>Carpenter</i> , 1996; <i>Clemetshaw et al.</i> , 1997; <i>Carslaw et al.</i> , 1997b; <i>Carpenter et al.</i> , 1998
BESSE	Bush Estate, Edinburgh, 1994	PERCA	15	Measurements systematically low compared with PSS Calculations	<i>Carpenter</i> , 1996

Table 1.1 (cont.)

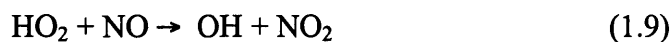
Campaign (Acronym)	Location, Year	Technique(s)	Midday max. [HO ₂] or [HO ₂ +ΣRO ₂] Observed /pptv	Comments	Reference (s)
SOAPEX 1	Cape Grim, Tasmania, 1995	PERCA	11	Relationships of peroxy radicals with <i>j</i> (O ¹ D) in clean and polluted air; O ₃ compensation point <i>ca</i> 25 pptv NO; CH ₃ O ₂ at night; winter / summer comparison; measurements systematically low by factor of 2	<i>Monks et al.</i> , 1996, 1998, 2000; <i>Carpenter et al.</i> , 1997; <i>Penkett et al.</i> , 1997; <i>Cox</i> , 1999
ATAPEX	Mace Head, Ireland, 1995	PERCA	5	Compensation point <i>ca</i> 50 pptv NO	<i>Carpenter et al.</i> , 1997
STRAT	Aircraft, 1995-6	FAGE (HO ₂)	N/A	Measurements in upper troposphere; acetone photolysis as major HO _x source in dry upper troposphere / lower stratosphere	<i>Jaeglé et al.</i> , 1997; <i>McKeen et al.</i> , 1997; <i>Wennberg et al.</i> , 1998
SUCCESS	Aircraft, 1996	FAGE (HO ₂)	N/A	HO ₂ /OH ratios 30% higher than modelled	<i>Brune et al.</i> , 1998; <i>Jaeglé et al.</i> , 1998
-	Aircraft, 1996	IM-RMS	N/A	4-8 km altitude; good agreement between measurements and steady-state calculations for clear skies	<i>Reiner et al.</i> , 1997, 1999
ACSOE-EASE	Mace Head, Ireland, 1996-7	FAGE (HO ₂), PERCA	8 (HO ₂), 25	PERCA results presented in this thesis; further submitted papers: <i>Carslaw et al.</i> , 2001a,b; <i>Monks et al.</i> , 2001; <i>Salisbury et al.</i> , 2001b	<i>Creasey et al.</i> , 1997; <i>Carslaw et al.</i> , 1999a, b, 2000; <i>Savage et al.</i> , 2001; <i>Salisbury et al.</i> , 2001a

Table 1.1 (cont.)

Campaign (Acronym)	Location, Year	Technique(s)	Midday max. [HO ₂] or [HO ₂ +ΣRO ₂] Observed /pptv	Comments	Reference (s)
SONEX	Aircraft, 1997	FAGE (HO ₂)	N/A	Effect of aircraft emissions in troposphere	<i>Brune et al.</i> , 1999; <i>Jaeglé et al.</i> , 1999, 2000; <i>Faloona et al.</i> , 2000
FREETEX	Jungfraujoch, Switzerland, 1996, 1998	PERCA	18	Seasonal comparison; photochemical control of diurnal ozone variation	<i>Zanis</i> , 1999; <i>Zanis et al.</i> , 1999, 2000a,b
-	Oki Island, Japan, 1998	FAGE (HO ₂)	14	HO ₂ observed at night	<i>Kanaya et al.</i> , 1999
BERLIOZ	Berlin, 1998	FAGE (HO ₂)	?	No results yet published	-
PROPHET	Michigan, 1998	FAGE (HO ₂)	?	No results yet published	-
SOAPEX 2	Cape Grim, Tasmania, 1999	FAGE (HO ₂), PERCA	8 (HO ₂); 20	PERCA results presented in this thesis	<i>Salisbury et al.</i> , 2001c
PUMA	Birmingham, 1999, 2000	FAGE (HO ₂)	?	No results yet published	-
PRIME	Ascot, 1999	FAGE (HO ₂), PERCA	?	No peroxy radical results yet published; response of OH concentrations to solar eclipse	<i>Abram et al.</i> , 2000

1.6 Introduction to the PERCA Technique

The PERCA technique was pioneered by *Cantrell et al.* [1982, 1984], and is based on the hydroperoxy (HO_2) radical catalysed oxidation of NO and CO to NO_2 and CO_2 respectively, as shown by the following reaction scheme:



Organic peroxy radicals (RO_2) are also detected by the PERCA instrument, since they are converted into HO_2 under the inlet reaction conditions. The net reaction occurring in the PERCA inlet may be represented by



so that the yield of both NO_2 (ΔNO_2) and CO_2 (ΔCO_2) is equal to CLN^* ($[\text{HO}_2] + [\text{RO}_2] + [\text{OH}]$), where the chain length, CLN, represents the number of HO_2/OH interconversion cycles which take place before radical termination occurs.

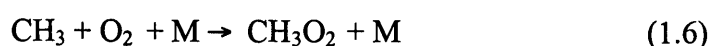
The PERCA instrument is based on NO_2 detection (see Chapter 2), and since $[\text{OH}] \ll [\text{HO}_2]$ and $[\text{RO}_2]$ in the boundary layer [e.g., *Mather et al.*, 1997], to a first approximation the PERCA chain length for measurement purposes is given by

$$\text{CLN} = \Delta\text{NO}_2 / \{[\text{HO}_2] + [\text{RO}_2]\} \quad (1.22)$$

Calibration of the PERCA instrument used in the present work is based on photolysis of a known concentration of methyl iodide (CH_3I) in dry, synthetic air to yield a known concentration of methylperoxy radicals:



$$(\lambda = 253.7\text{nm})$$



However, recent work by *Mihele and Hastie* [1998] and *Mihele et al.* [1999] suggests that the PERCA chain length is substantially reduced in humid air, so that field calibrations performed

under dry conditions are likely to overestimate the operating chain length of the instrument, which in turn will lead to underestimation of the peroxy radical mixing ratios in the atmosphere. Such an effect was indeed observed during the SOAPEX 1 experiment, where the PERCA instrument measured systematically low by a factor of two, based on two independent criteria [Monks *et al.*, 1998]. In an effort to quantify the magnitude of the chain-length reduction in humid air, extensive laboratory experiments have been conducted with the UEA-Leicester PERCA instrument in the course of this work; the results of these experiments are presented in Chapter 2.

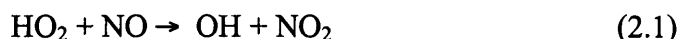
1.7 Summary

This chapter has introduced the broad structure of the Earth's lower atmosphere, and the basic photochemistry, which to a large extent controls the levels of a wide variety of trace species. The different techniques used to measure peroxy radicals in the atmosphere have been briefly reviewed, and an overview of previous measurements, including some of the main published conclusions on peroxy radical chemistry, has been presented (Table 1.1). The structure of the rest of this thesis is based on two parallel lines of enquiry: first, laboratory investigation of the PERCA CLN-humidity effect outlined in the last section (Chapter 2); second, analysis of the peroxy radical data sets obtained from three field campaigns, two at Mace Head in Ireland (EASE 96, EASE 97), and one at Cape Grim in Tasmania (SOAPEX 2) (Chapters 3-5). The analyses of the PERCA EASE 96, EASE 97 and SOAPEX 2 data have been carried out allowing for a possible underestimation of peroxy radical mixing ratios, where necessary (see Chapters 3-5). In Chapter 6, the results of the laboratory characterisation experiments are applied to the experimental data sets, in order to assess whether the theoretical humidity correction to the PERCA data is applicable in the real atmosphere. Finally, Chapter 7 summarises the main findings of Chapters 2-6, and includes suggestions for further research with the PERCA instrument.

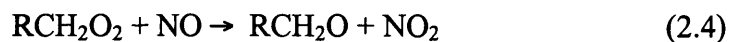
Chapter 2 – Experimental Techniques and Characterisation of the PERCA Instrument in Humid Air

2.1 Introduction

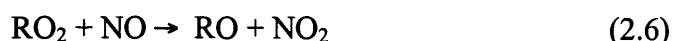
The Peroxy Radical Chemical Amplification (PERCA) technique for the measurement of hydroperoxy (HO_2) and the sum of the organic peroxy radicals (ΣRO_2) was pioneered by *Cantrell et al.*, [1982, 1984]. The technique depends on the HO_2 catalysed oxidation of NO and CO to NO_2 and CO_2 , respectively (reactions 2.1-2.3).



Organic peroxy radicals are also detected by the PERCA technique, since they are converted into HO_2 under the PERCA inlet reaction conditions. For primary organic peroxy radicals the following reaction sequence occurs:



For secondary and tertiary peroxy radicals the chemistry is more complex, but the general process may be represented by

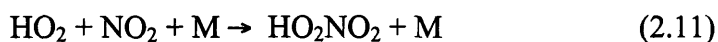
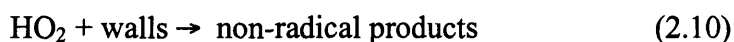
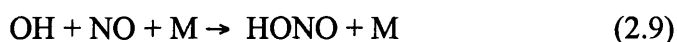


It follows that the net reaction occurring in the PERCA instrument inlet may be represented by



so that the yield of both NO_2 (ΔNO_2) and CO_2 (ΔCO_2) is equal to $\text{CLN} \cdot ([\text{HO}_2] + [\text{RO}_2] + [\text{OH}])$, where the chain length, CLN (sometimes called the instrument

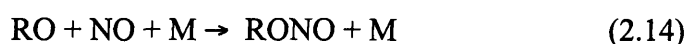
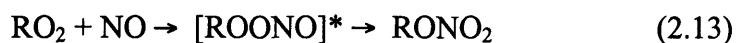
‘amplification factor’), represents the number of HO₂/OH interconversion cycles which take place before radical termination occurs, essentially *via* reactions (2.9)-(2.11):[†]



Since [OH] << [HO₂] and [RO₂] in the planetary boundary layer [*e.g.*, Mather *et al.*, 1997], to a first approximation the PERCA chain length (CLN) is given by

$$\text{CLN} = \Delta\text{NO}_2 / \{[\text{HO}_2] + [\text{RO}_2]\} \quad (2.12)$$

A complication arises, however, in that the fractional conversion of RO₂ into HO₂ varies with the size and structure of the organic group [*Clemmitshaw et al.*, 1997; *Ashbourn et al.*, 1998]. Under the standard operating conditions of the PERCA instrument, with *ca* 3 ppmv (parts per million by volume) NO present in the inlet, competing reactions of RO₂ and RO (alkoxy) radicals with NO to form organic nitrates and nitrites occur alongside the chain-propagation reactions (2.6) and (2.7):



Nevertheless, for structurally simple RO such as CH₃O, production of HO₂ occurs in a concerted manner *via* reaction with O₂ [*Atkinson*, 1994], and the fractional conversion of RO₂ into HO₂ is relatively high (0.85 for CH₃O₂ [*Clemmitshaw et al.*, 1997]).

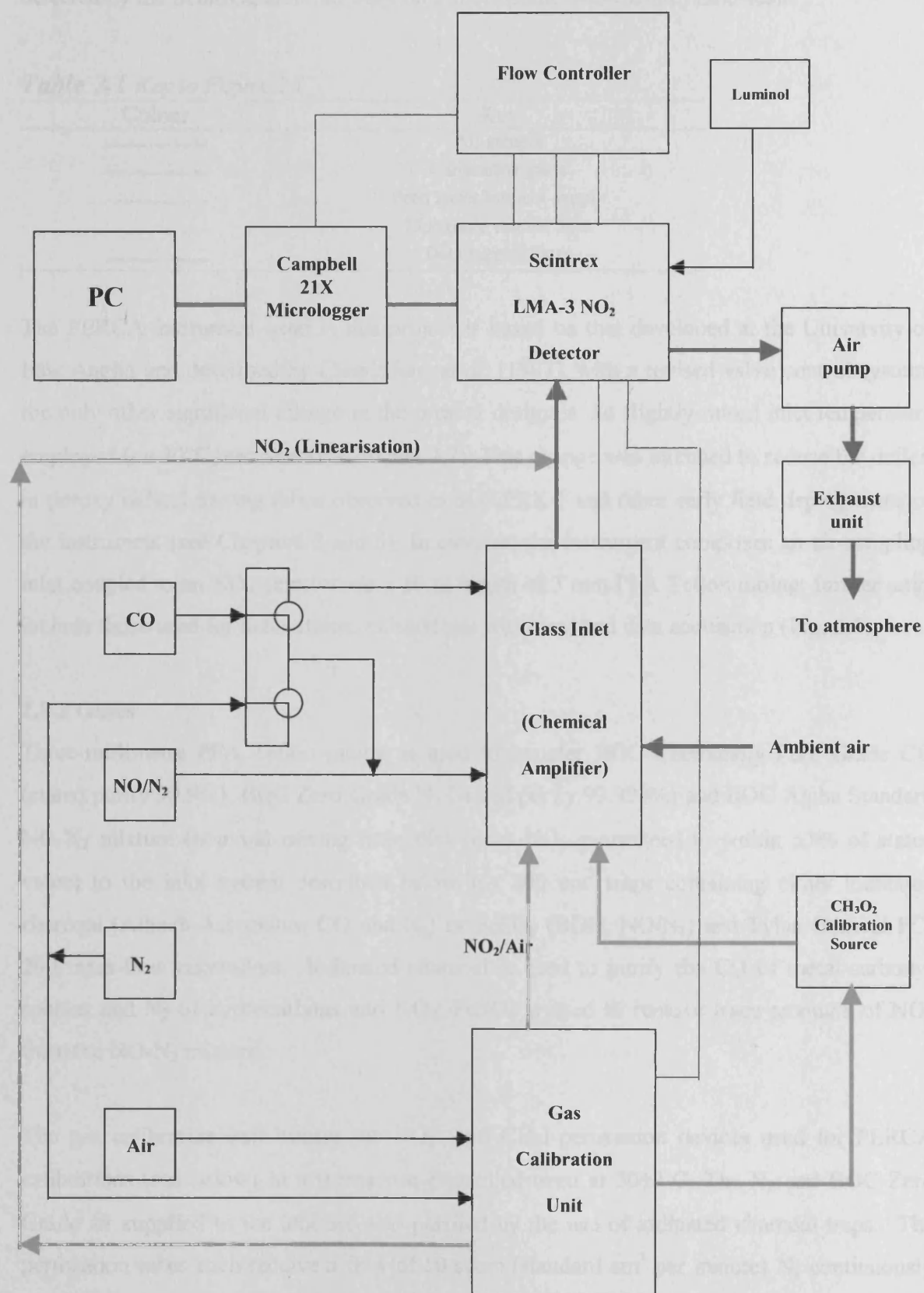
2.2 Instrument Description

2.2.1 Introduction to the UEA-Leicester PERCA instrument

A schematic of the UEA-Leicester PERCA instrument is shown in Figure 2.1, where the line colours have the meanings given in Table 2.1. The instrument is based on detection of the NO₂ produced in the peroxy radical catalysed chain reaction described in the last section; knowledge of the chain-length (CLN) then allows calculation of the ambient peroxy radical

[†] A further gas-phase loss process has recently been postulated for HO₂; this point is discussed in Section 2.6.

Figure 2.1 Schematic representation of the UEA-Leicester PERCA instrument



mixing ratios (Section 2.4). Measurements are modulated, *i.e.* periods of amplification of the radical signal are alternated with periods where the radicals are allowed to terminate in the inlet. This is to account for ambient ozone and nitrogen dioxide concentrations, since both are detected by the Scintrex, and may vary on a short (minute-to-minute) time-scale.

Table 2.1 Key to Figure 2.1

Colour	Key
	Air sample
	Calibration gases
	Feed gases/luminol supply
	Electronic control lines
	Data logging lines

The PERCA instrument used in this project is based on that developed at the University of East Anglia and described by *Clemitshaw et al.* [1997], with a revised valve control system; the only other significant change in the present design is the slightly raised inlet temperature employed (*ca* 30°C; see Sections 2.6 and 2.7). This change was intended to reduce the deficit in peroxy radical mixing ratios observed in SOAPEX 1 and other early field deployments of the instrument (see Chapters 5 and 6). In essence, the instrument comprises an air-sampling inlet coupled to an NO₂ detector *via* a 16 m length of 3 mm PFA Teflon tubing; further units include those used for calibrations, exhaust-gas treatment and data acquisition (Fig. 2.1).

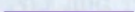
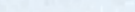
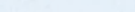
2.2.2 Gases

Three-millimetre PFA Teflon tubing is used to transfer BOC Chemically Pure Grade CO (stated purity 99.9%), BOC Zero Grade N₂ (stated purity 99.998%) and BOC Alpha Standard NO-N₂ mixture (nominal mixing ratio 600 ppmv NO; guaranteed to within $\pm 1\%$ of stated value) to the inlet system described below *via* 200 cm³ traps containing either iodinated charcoal (Alltech Associates; CO and N₂) or FeSO₄ (BDH; NO/N₂) and Tylan General FC-260 mass-flow controllers. Iodinated charcoal is used to purify the CO of metal-carbonyl species and N₂ of hydrocarbons and NO₂; FeSO₄ is used to remove trace amounts of NO₂ from the NO-N₂ mixture.

The gas calibration unit houses the NO₂- and CH₃I-permeation devices used for PERCA calibrations (see below) in a thermostat-controlled oven at 30 $\pm$ 2°C. The N₂ and BOC Zero Grade air supplied to the unit are also purified by the use of iodinated charcoal traps. The permeation tubes each receive a flow of 50 sccm (standard cm³ per minute) N₂ continuously when the PERCA is in operation in order to ensure that their outputs are as stable as possible.

mixing ratios (Section 2.4). Measurements are modulated, *i.e.* periods of amplification of the radical signal are alternated with periods where the radicals are allowed to terminate in the inlet. This is to account for ambient ozone and nitrogen dioxide concentrations, since both are detected by the Scintrex, and may vary on a short (minute-to-minute) time-scale.

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2.2.2 Gases

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The gas calibration unit houses the NO₂- and CH₃I-permeation devices used for PERCA calibrations (see below) in a thermostat-controlled oven at 30 $\pm$ 2°C. The N₂ and BOC Zero Grade air supplied to the unit are also purified by the use of iodinated charcoal traps. The permeation tubes each receive a flow of 50 sccm (standard cm³ per minute) N₂ continuously when the PERCA is in operation in order to ensure that their outputs are as stable as possible.

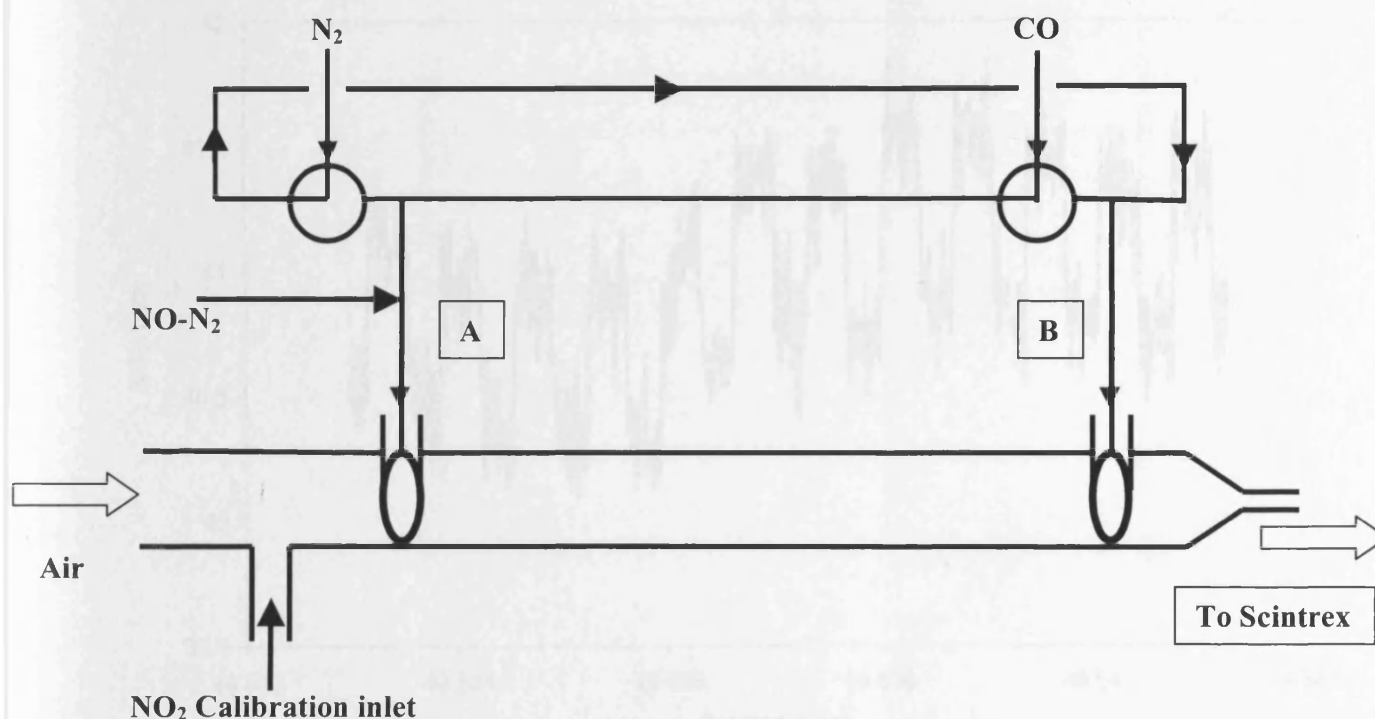
The tubes are weighed at regular intervals using a 4-figure balance to keep a continual check on their actual outputs, including immediately before and after a field campaign.

The exhaust from the air pump contains *ca* 6% by volume CO and 3 ppmv NO_x (NO+NO₂) and is treated by passage through a series of 1 L Pyrex traps. The first trap contains type 5A molecular sieve to dry the mixture; the second contains Hopcalite (Molecular Products), which oxidises CO to CO₂; the third trap contains Sofnofil (Molecular Products), which adsorbs NO and NO₂. When not in use, the outputs of the permeation devices in N₂ are purified by passage through 200 cm³ traps containing molecular sieve and Sofnofil.

When the PERCA instrument is in operation, the ambient CO levels are continuously monitored using an Oldham model TX 11 CO toximeter to guard against leaks and to check that the exhaust unit is performing efficiently.

2.2.3 The PERCA inlet – mode of operation

A schematic of the UEA-Leicester PERCA inlet is shown in Figure 2.2. The inlet consists of a Pyrex glass tube fitted with three side arms. The side arms are attached to a set of solenoid valves *via* catheterised Teflon fittings and $\frac{1}{8}$ th-inch Teflon tubing; the connections are kept as short as possible in order to minimise dead space. The first side arm is used to introduce a standard NO₂-zero air mixture to the inlet for calibration of the Scintrex (see Section 2.3). The other two side arms are used for the addition of NO, CO and N₂ to the inlet in both calibration and measurement modes. Addition of CO and NO together at point A corresponds to the instrument amplification phase, lasting 24 seconds of a 1-minute cycle. Solenoid valves control the switching between this and the termination phase, where the addition of CO is delayed until the radicals have been terminated (point B). Nitrogen is used to balance the gas flow rates between the addition points in order to avoid pressure pulsing within the inlet. The termination phase also lasts 24 seconds; the other 12 seconds of each minute cycle represent the time allowed for switching of the inlet gases in the feed-lines: 6 seconds for each change-over. The solenoid valves controlling the cycle are activated automatically by the Campbell 21X Micrologger used to log the PERCA data (see Section 2.2.5). The inlet is 25 mm in diameter and *ca* 180mm in length, with a distance of 125 mm between side arms A and B. The inlet gases enter the inlet *via* tori running around the circumference of the inlet and pierced by eight holes of diameter *ca* 2 mm; this system is designed to promote rapid mixing of the inlet gases with the sampled airflow.

Figure 2.2 The PERCA inlet

During the SOAPEX 2 campaign (Chapter 5), the PERCA inlet was deployed on a wooden trolley positioned on a purpose-built steel mount suspended from the top of the wall of the Cape Grim research station. The unit could be pushed out well away (*ca* 2 m) from the wall during ambient measurements, and pulled in adjacent to the wall for peroxy radical calibrations and general maintenance, as required.

Examples of the NO₂ modulations obtained during SOAPEX 2 are shown in Figure 2.3, where the variation in the NO₂ background level (or more accurately [NO₂]+[O₃], see Section 2.3) is clearly apparent. Figure 2.4 shows an entire peroxy radical diel cycle (1 min averaged data), showing a typical build-up of peroxy radicals during the morning, with peak mixing ratios occurring at around the solar maximum, and a decrease in the course of the afternoon towards minimum levels at night. The photolysis frequency of ozone, $j(\text{O}^1\text{D})$, is also plotted in Figure 2.4 for comparison. The rapid response of peroxy radical levels to changes in $j(\text{O}^1\text{D})$ is clearly shown in Fig. 2.4: see especially the suppression of peroxy radical mixing ratios at around 12pm, 4pm and 5pm AEST (Australian Eastern Standard Time) due to increased cloud cover at these times.

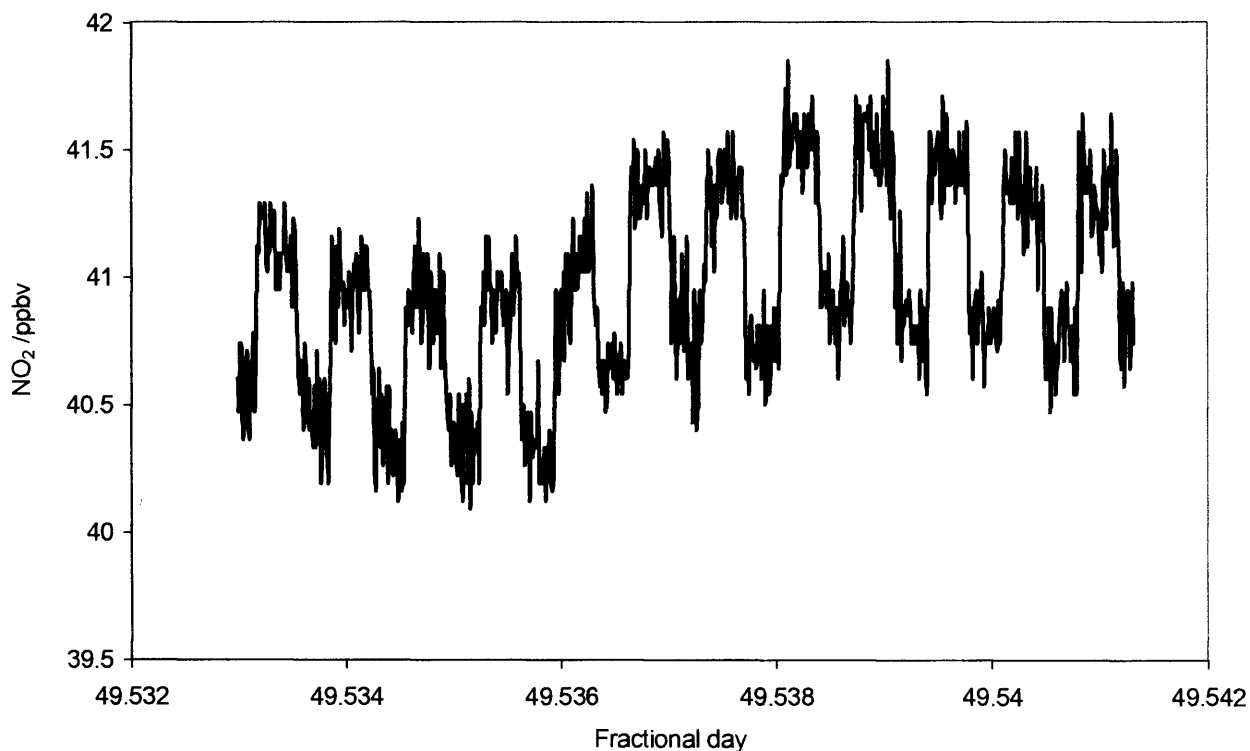
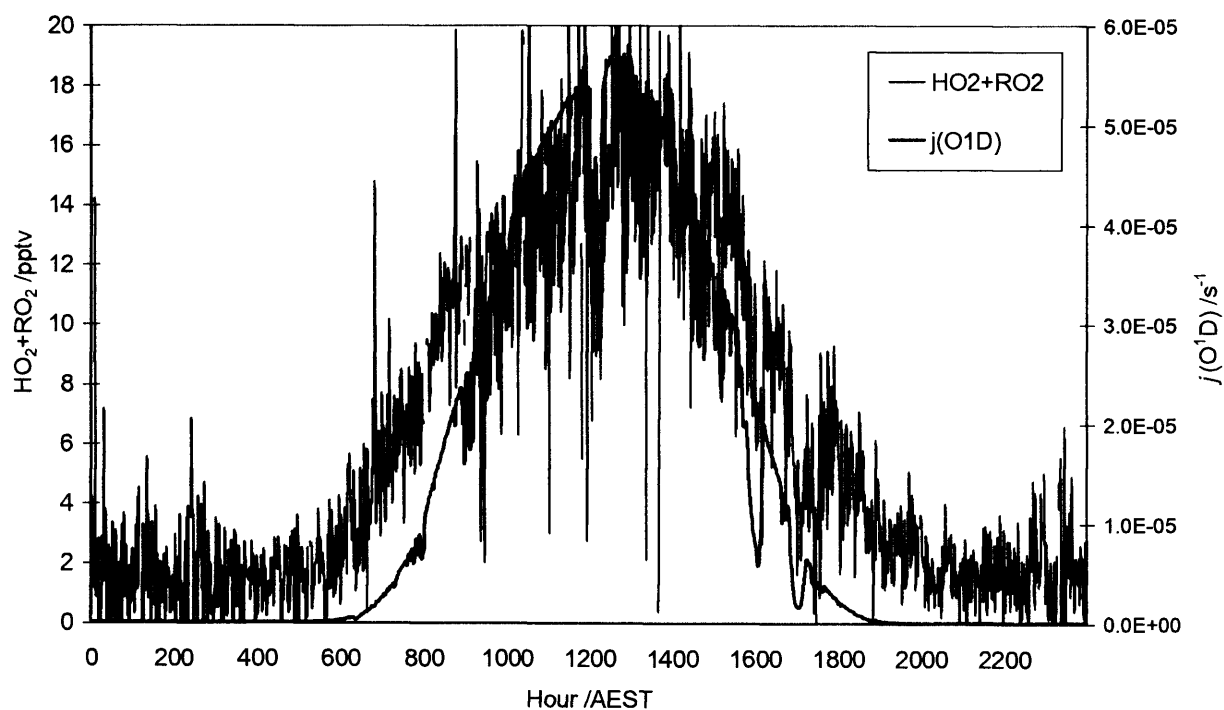
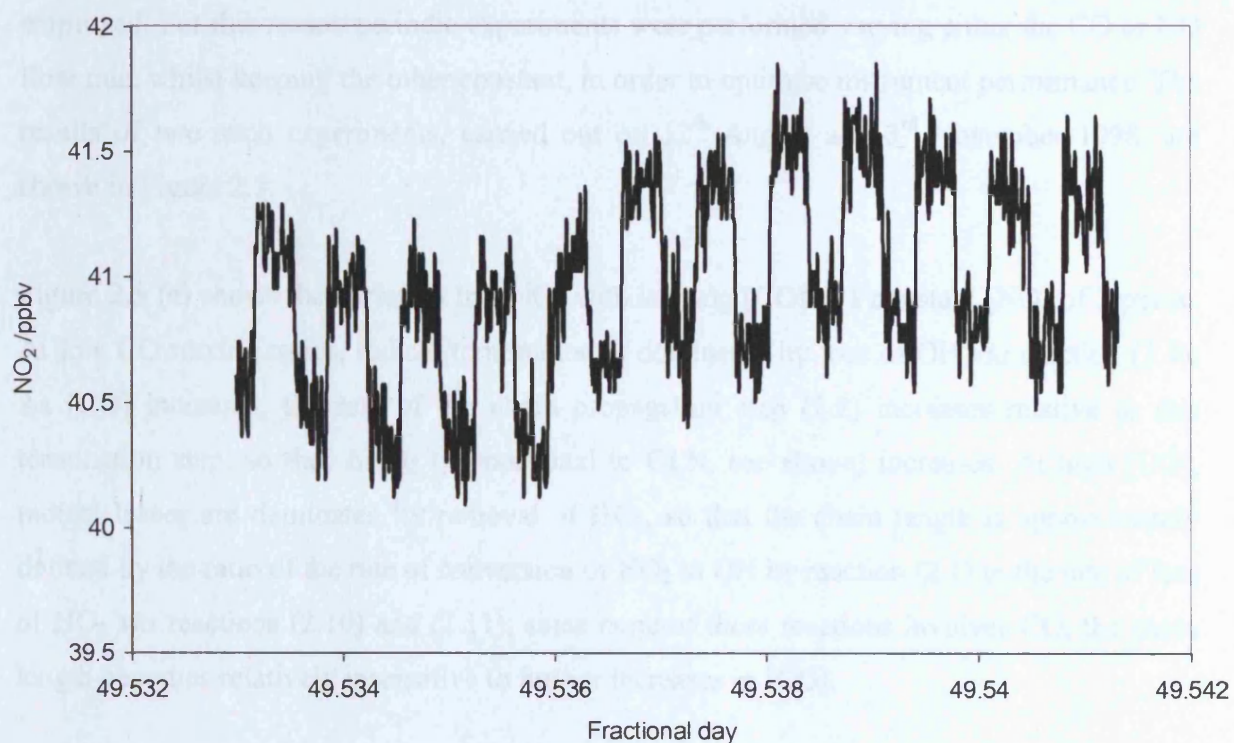
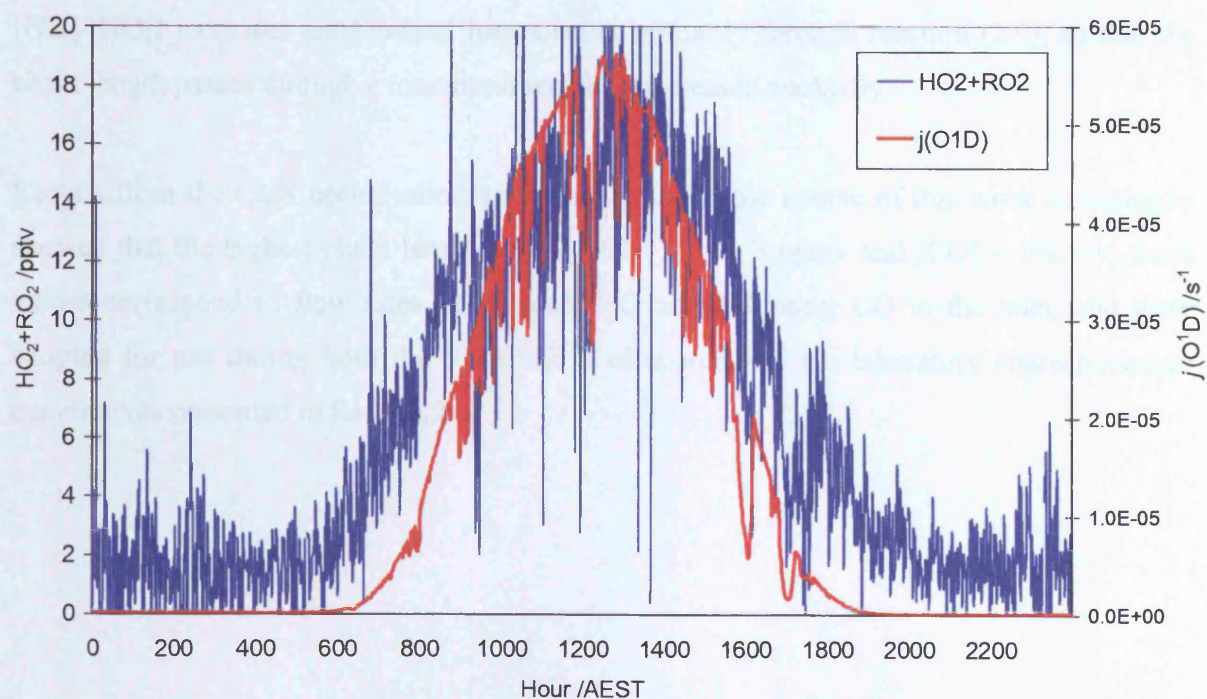
Figure 2.3 PERCA modulations from 18th February 1999 during SOAPEX 2**Figure 2.4** Peroxy radical data from 19th January 1999 during SOAPEX 2 (1 min averages)

Figure 2.3 PERCA modulations from 18th February 1999 during SOAPEX 2**Figure 2.4** Peroxy radical data from 19th January 1999 during SOAPEX 2 (1 min averages)

2.2.4 Chain length optimisation

The chain length of the PERCA instrument is affected by the CO and NO concentrations employed. For this reason periodic experiments were performed varying either the CO or NO flow rate, whilst keeping the other constant, in order to optimise instrument performance. The results of two such experiments, carried out on 12th August and 3rd November 1998, are shown in Figure 2.5.

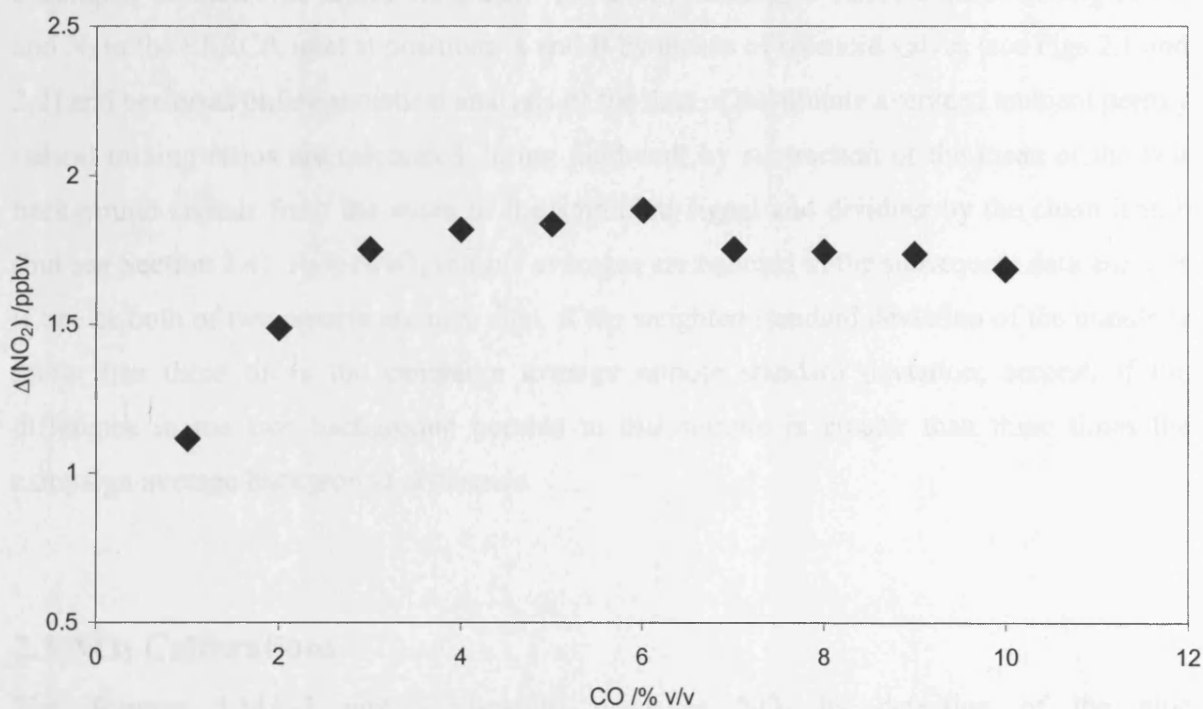
Figure 2.5 (a) shows the variation in ΔNO_2 with varying $[\text{CO}]$ at a constant $[\text{NO}]$ of 3 ppmv. At low CO mixing ratios, radical termination is dominated by loss of OH *via* reaction (2.9). As $[\text{CO}]$ increases, the rate of the chain propagation step (2.2) increases relative to this termination step, so that ΔNO_2 (proportional to CLN, see above) increases. At high $[\text{CO}]$, radical losses are dominated by removal of HO_2 , so that the chain length is approximately defined by the ratio of the rate of conversion of HO_2 to OH by reaction (2.1) to the rate of loss of HO_2 *via* reactions (2.10) and (2.11); since none of these reactions involves CO, the chain length becomes relatively insensitive to further increases in $[\text{CO}]$.

Similarly, Figure 2.5 (b) shows an NO optimisation experiment with $[\text{CO}]$ constant at 6% volume per volume (v/v). At low $[\text{NO}]$ (with high enough $[\text{CO}]$ that radical losses are dominated by HO_2 removal), as $[\text{NO}]$ increases, the rate of reaction (2.1) increases relative to (2.10) and (2.11), so that the chain length increases. As $[\text{NO}]$ increases further, the ratio $[\text{OH}]/[\text{HO}_2]$ increases until radical losses occur primarily through reaction (2.9), so that the chain length passes through a maximum and then decreases markedly.

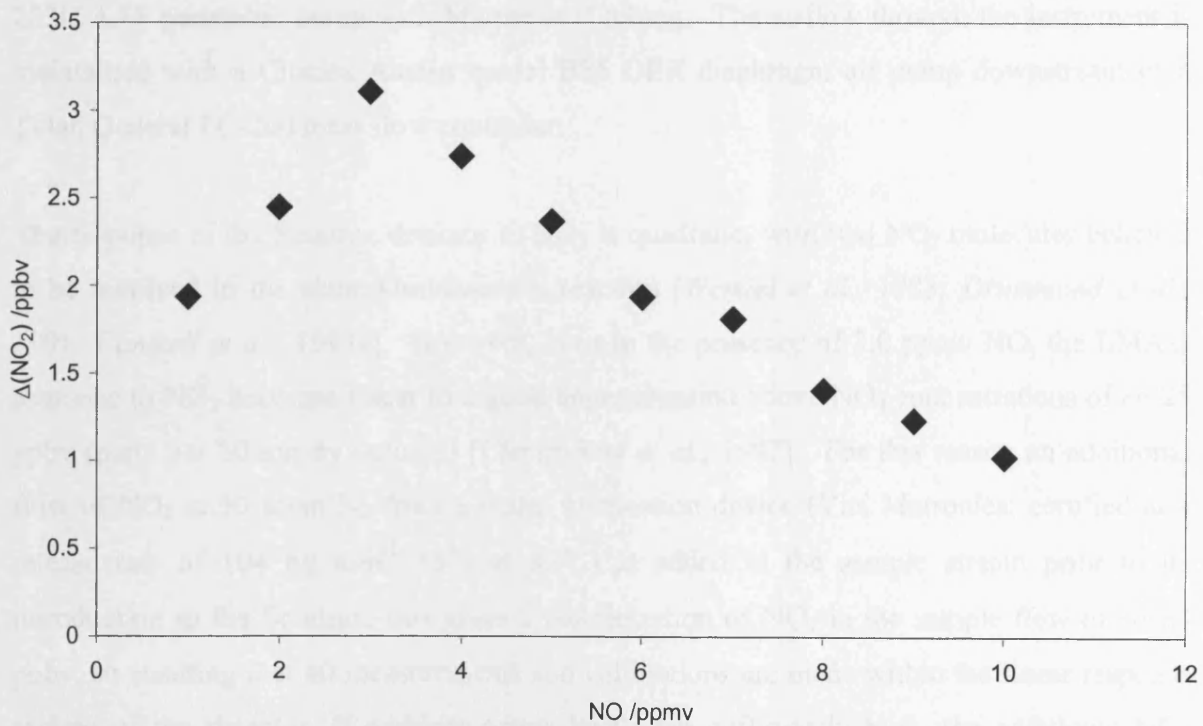
Results from the CLN optimisation experiments during the course of this work consistently showed that the highest chain lengths occur with $[\text{NO}] = 3$ ppmv and $[\text{CO}] = 6\%$ v/v; these values correspond to flow rates of 10 sccm NO and 120 sccm CO in the inlet, and were adopted for use during both the SOAPEX 2 campaign and the laboratory characterisation experiments presented in Section 2.6.

Figure 2.5 Chain length optimisation experiments

(a) Variation of CO at constant NO (3 ppmv) [12th August 1998]



(b) Variation of NO at constant CO (6% v/v) [3rd November 1998]



2.2.5 Data Acquisition

The PERCA data are logged at 1 Hz using a Campbell Scientific 21X Micrologger with a 16-bit analogue-to-digital converter, and collected every 15 minutes by automated interface with a Compaq Contura 3/25 laptop computer. The 21X Micrologger controls the switching of CO and N₂ to the PERCA inlet at positions **A** and **B** by means of solenoid valves (see Figs 2.1 and 2.2) and performs online statistical analysis of the data. One-minute averaged ambient peroxy radical mixing ratios are calculated during fieldwork by subtraction of the mean of the two background signals from the mean of the amplified signal and dividing by the chain length (but see Section 2.4). Raw ΔNO_2 minute averages are rejected in the subsequent data analysis if one or both of two criteria are met: first, if the weighted standard deviation of the minute is more than three times the campaign average minute standard deviation; second, if the difference in the two background periods in that minute is greater than three times the campaign average background difference.

2.3 NO₂ Calibrations

The Scintrex LMA-3 unit (Unisearch) measures NO₂ by detection of the blue chemiluminescence produced during the reaction between NO₂ and a proprietary solution containing luminol (5-amino-2,3-dihydro-1,4-phthalazinedione). The luminol is maintained at a continuous flow rate of 0.2 mL min⁻¹ through the Scintrex using a Watson Marlow model 202U/AA8 peristaltic pump with Marprene II tubing. The airflow through the instrument is maintained with a Charles Austen model B85 DER diaphragm air pump downstream of a Tylan General FC-260 mass flow controller.

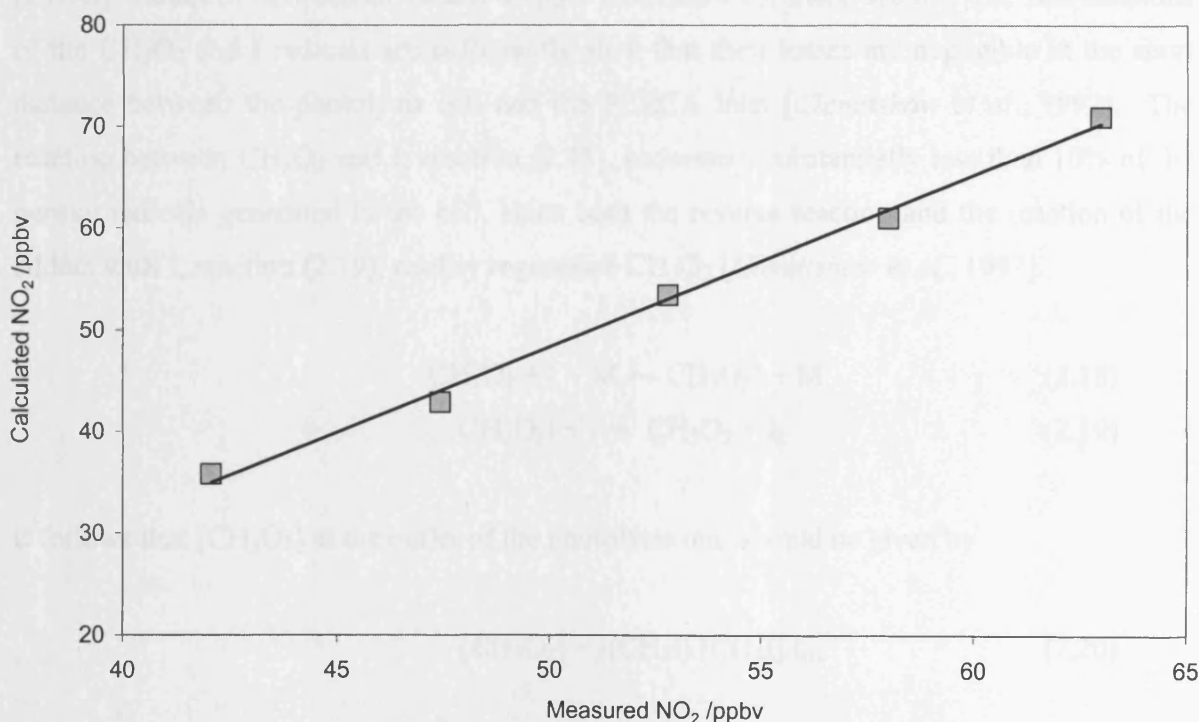
The response of the Scintrex detector to NO₂ is quadratic, with two NO₂ molecules believed to be involved in the chemiluminescence reaction [Wendel *et al.*, 1983; Drummond *et al.*, 1991; Cantrell *et al.*, 1993a]. However, even in the presence of 3.0 ppmv NO, the LMA-3 response to NO₂ becomes linear to a good approximation above NO₂ concentrations of *ca* 25 ppbv (parts per billion by volume) [Clemetshaw *et al.*, 1997]. For this reason an additional flow of NO₂ in 50 sccm N₂ from a wafer permeation device (Vici Metronics; certified at a release rate of 104 ng min⁻¹ $\pm$ 5% at 30°C) is added to the sample stream prior to its introduction to the Scintrex; this gives a concentration of NO₂ in the sample flow of *ca* 35 ppbv, so ensuring that all measurements and calibrations are made within the linear response regime of the detector. If ambient ozone levels are sufficiently high, the additional NO₂

(known as NO₂ linearisation or NO₂ lin) may not be required, since ozone is titrated to NO₂ by the NO present in the sample stream during transport between the inlet and the Scintrex:



Multipoint NO₂ calibrations are carried out regularly during PERCA operation to assess the performance of the detection system. Zero air at various flow rates is blended with a stream of 50 sccm N₂ carrying the output of a second NO₂ wafer permeation device (Vici Metronics) with a certified leak-rate of 417 ng min⁻¹ ±5% at 30°C. The blended gas stream is introduced to the inlet *via* the calibration side arm, as indicated in Fig. 2.2. Airflows of between 3.0 and 6.0 standard litres per minute (sLpm) give [NO₂] values of between *ca* 35 and 70 ppbv, which are representative of the usual operating range of the Scintrex. 2.0 sLpm of the mixture is generally sampled by the detector; the excess is allowed to vent out of the bottom of the inlet. A plot of the calculated (based on the leak-rate of the NO₂ permeation tube and the airflow) *versus* the actual measured NO₂ mixing ratios gives an immediate test of the linear response of the instrument. Figure 2.6 shows one such plot, using data collected on 6th February 1999 during SOAPEX 2 (see Chapter 5).

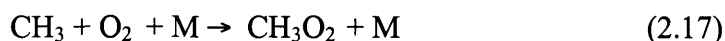
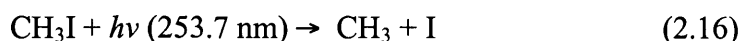
Figure 2.6 NO₂ calibration on 6th February 1999 during SOAPEX 2



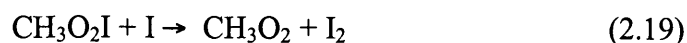
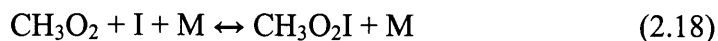
2.4 Peroxy Radical Calibrations

2.4.1 Calibration method

The UEA-Leicester PERCA instrument uses a photolytic source of methylperoxy (CH_3O_2) radicals to enable chain length determinations to be carried out regularly during measurement campaigns in the field. The output of a methyl iodide permeation device in 50 sccm of nitrogen is blended with between 3.5 and 5.5 sLpm of air and passed through a quartz cell placed adjacent to a Philips 15W, model TUV G15T8 low-pressure mercury lamp. Both the cell (TSL Quadrant) and lamp are housed in a weatherproof aluminium casing, which is placed on a shelf below the PERCA inlet when in use. The outlet of the calibration cell is connected to the glass inlet *via* a 6 cm length of 6 mm o.d. PFA Teflon tubing so that the tube end is *ca* 5 mm inside the inlet. Methyl iodide is photolysed, and the resulting methyl radicals react with oxygen in the zero air to produce methylperoxy radicals:



The certified output of the CH_3I permeation tube is $217 \pm 5 \text{ ng min}^{-1}$ at 30°C , although the measured leak rate has been somewhat lower in practice, at 197 ng min^{-1} ; this gives calculated $[\text{CH}_3\text{O}_2]$ values of between *ca* 18 and 44 pptv (see below for more details). The self-reactions of the CH_3O_2 and I radicals are sufficiently slow that their losses are negligible in the short distance between the photolysis cell and the PERCA inlet [Clemmitshaw *et al.*, 1997]. The reaction between CH_3O_2 and I, reaction (2.18), sequesters substantially less than 10% of the peroxy radicals generated in the cell, since both the reverse reaction and the reaction of the adduct with I, reaction (2.19), readily regenerate CH_3O_2 [Clemmitshaw *et al.*, 1997].



It follows that $[\text{CH}_3\text{O}_2]$ at the outlet of the photolysis unit should be given by

$$[\text{CH}_3\text{O}_2] = j(\text{CH}_3\text{I}) \cdot [\text{CH}_3\text{I}] \cdot t_{\text{res}} \quad (2.20)$$

assuming no heterogeneous wall losses of CH_3O_2 in the cell itself, where $j(\text{CH}_3\text{I})$ is the photolysis rate of CH_3I (determined as described in the next section) and t_{res} is the residence

time in the cell. *Clemmitshaw et al.* [1997] tested the assumption of zero wall losses in the photolysis cell by generating CH_3O_2 radicals in one photolysis unit and then passing the radicals so formed (1) directly into the PERCA inlet, then (2) *via* a second quartz cell of the same dimensions [see also *Carpenter*, 1996]. In this fashion a mean heterogeneous wall-loss rate of $12.7 \pm 2.0\% \text{ s}^{-1}$ for total gas flow-rates of 3.05, 4.05 and 5.05 sLpm (equivalent to t_{res} 1.22–0.74 s) was measured. The revised expression for $[\text{CH}_3\text{O}_2]$ therefore becomes

$$[\text{CH}_3\text{O}_2] = j(\text{CH}_3\text{I})[\text{CH}_3\text{I}]t_{\text{res}}(1 - 0.127t_{\text{res}}/2) \quad (2.21a)$$

or
$$[\text{CH}_3\text{O}_2] = 5.0 \times 10^{-3} [\text{CH}_3\text{I}]t_{\text{res}}(1 - 0.127t_{\text{res}}/2) \quad (2.21b)$$

which assumes an average residence time of $t_{\text{res}}/2$ for CH_3O_2 radicals generated in the cell (see also next section) [*Carpenter*, 1996; *Clemmitshaw et al.*, 1997]. Measured chain lengths are defined with respect to HO_2 radicals (see Section 2.1). Given that 0.85 is the fractional conversion of CH_3O_2 to HO_2 at the $[\text{NO}]$ value of 3 ppmv present in the inlet [*Clemmitshaw et al.*, 1997], the actual chain length is given by

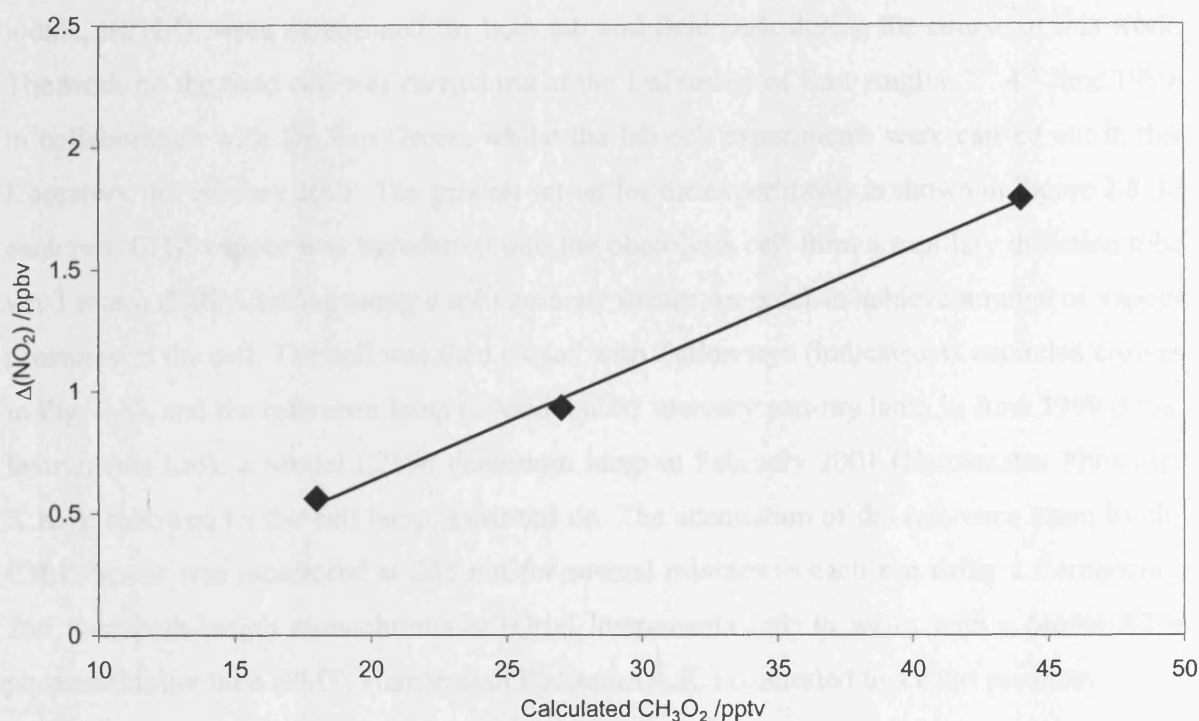
$$\text{CLN} = \Delta\text{NO}_2 / \{0.85[\text{CH}_3\text{O}_2]\} \quad (2.22)$$

During fieldwork, the PERCA instrument is calibrated every 5-7 days of operation using total flow-rates of 3.55, 4.55 and 5.55 sLpm; the measured chain lengths are independent of $[\text{CH}_3\text{O}_2]$ within experimental error [*Clemmitshaw et al.*, 1997]. A plot of one such chain length determination, performed on 31st January 1999 during SOAPEX 2, is given in Figure 2.7.

2.4.2 Photolysis cell wall-loss experiments

Two CH_3I photolysis units are used in the current PERCA instrument set-up. The first unit remains in the laboratory, and to date has been used as a standard in order to calibrate the second unit, which is specifically designed to be used in the field. In the discussion that follows, the first unit will be referred to as the lab cell, whereas the second will be referred to as the field cell.

The cell wall-loss experiments reported by *Clemmitshaw et al.* [1997] were carried out on the lab cell. Similar experiments performed in this laboratory in 1998 and 1999 on the field cell gave slightly different results (Table 2.2), with a mean heterogeneous wall-loss rate of $9.7 \pm 1.9\% \text{ s}^{-1}$ for total gas flow-rates of 3.55, 4.55 and 5.55 sLpm (t_{res} 1.74-1.22 s).

Figure 2.7 Chain length determination on 31st January 1999 during SOAPEX 2

However, the two photolysis cells are of different dimensions: lab cell volume 62.8 cm³; calculated internal surface area 125.7 cm²; field cell volume 103.5 cm³, calculated internal surface area 159.3 cm². If the wall-loss rate is assumed to be proportional to the surface area (SA)/volume (V) ratio for each cell, the expected ratio of wall-loss rates for the two cells (Lab = L, Field = F) is given by

$$\text{Wall-loss rate ratio (lab/field)} = (\text{SA}_L \cdot V_F) / (\text{SA}_F \cdot V_L) = (125.7 \times 103.5) / (159.3 \times 62.8) = 1.3.$$

The average measured ratio was $(12.7/9.7) = 1.3$.

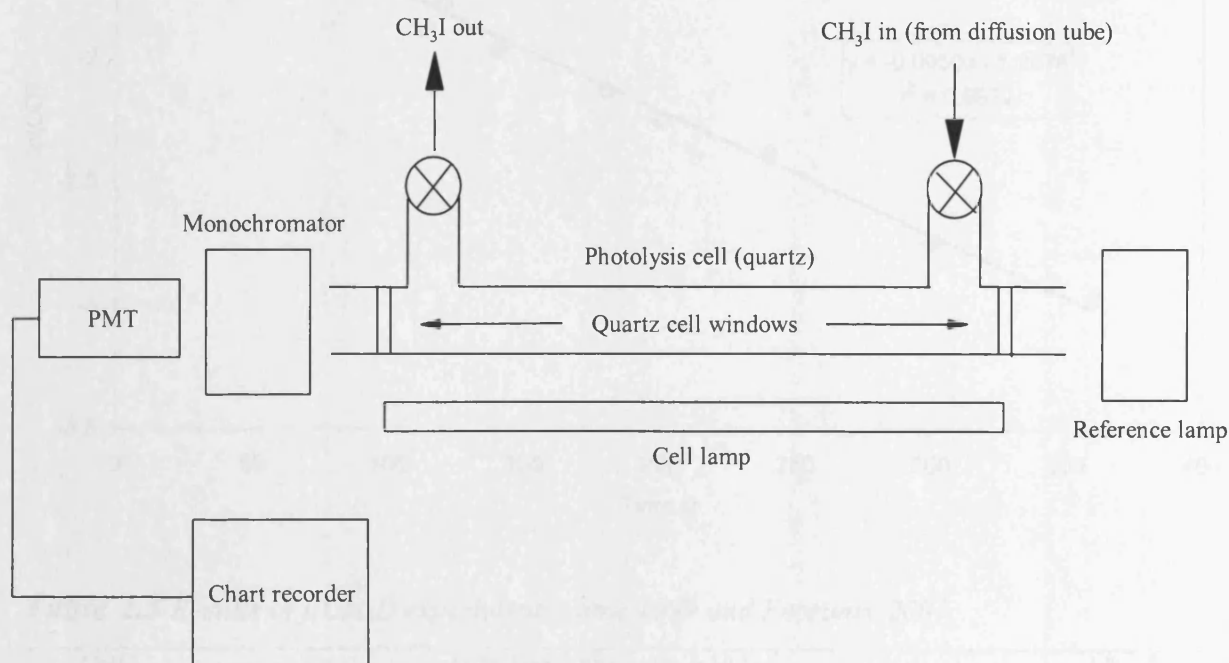
Table 2.2 Cell wall-loss experiment results (field calibration cell)

Date of experiment	Airflow /sLpm	Residence time /s	Measured wall-loss /%	Wall-loss rate /s ⁻¹
29/7/98	3.55	1.74	9.2	5.3
	4.05	1.53	7.4	4.8
	4.55	1.36	12.4	9.1
30/7/98	4.55	1.36	25.2	18.5
	5.05	1.22	11.3	9.3
10/8/99	3.55	1.74	20.7	11.9
12/8/99	3.55	1.74	15.8	9.1

2.4.3 $j(\text{CH}_3\text{I})$ determinations

Following the general procedure adopted by *Carpenter* [1996], the photolysis rates of methyl iodide, $j(\text{CH}_3\text{I})$, were determined for both lab and field cells during the course of this work. The work on the field cell was carried out at the University of East Anglia, 3rd-4th June 1999, in collaboration with Dr Tim Green, whilst the lab cell experiments were carried out in this laboratory in February 2001. The general set-up for the experiments is shown in Figure 2.8. In each run, CH_3I vapour was transferred into the photolysis cell from a capillary diffusion tube via 3 mm o.d. PFA tubing using a split zero air stream, in order to achieve a range of vapour pressures in the cell. The cell was then closed with Teflon taps (indicated as encircled crosses in Fig. 2.8), and the reference lamp (a Model 6035 mercury pen-ray lamp in June 1999 (Oriol Instruments Ltd); a Model L2196 deuterium lamp in February 2001 (Hamamatsu Photonics K.K.)), followed by the cell lamp, switched on. The attenuation of the reference beam by the CH_3I vapour was monitored at 265 nm for several minutes in each run using a Cornerstone 260 ¼-m path-length monochromator (Oriol Instruments Ltd) in series with a Model R374 photomultiplier tube (PMT; Hamamatsu Photonics K.K.) connected to a chart recorder.

Figure 2.8 Schematic representation of the apparatus used in the $j(\text{CH}_3\text{I})$ determinations



The initial concentration of CH_3I in the cell could be calculated for each experiment using the Beer-Lambert law:

$$\ln(I_0/I) = \text{OD} = \sigma[\text{CH}_3\text{I}]l \quad (2.23)$$

where I_0 is the intensity of the reference beam with no CH_3I present, I is the intensity of the reference beam with CH_3I present, OD is the optical density, σ is the absorption cross-section of CH_3I at 265 nm ($10.33 \times 10^{-19} \text{ cm}^2 \text{ mol}^{-1}$) [Jenkin *et al.*, 1993], and l is the optical path length (20 cm for each cell).

The range of $[\text{CH}_3\text{I}]$ values used was *ca* 400-1200 ppmv, corresponding to *ca* 20-50% attenuation of the reference beam. Since OD is proportional to $[\text{CH}_3\text{I}]$ (Equation 2.23), a plot of $\ln(\text{OD})$ against time could be used to find $j(\text{CH}_3\text{I})$ using standard first-order kinetics; an example of such a plot (from 15th February 2001) is shown in Figure 2.9. The full results of both sets of experiments are given in Table 2.3. No evidence of CH_3I photolysis by the reference lamp was observed in either set of experiments.

Figure 2.9 Example $j(\text{CH}_3\text{I})$ determination (15th February 2001)

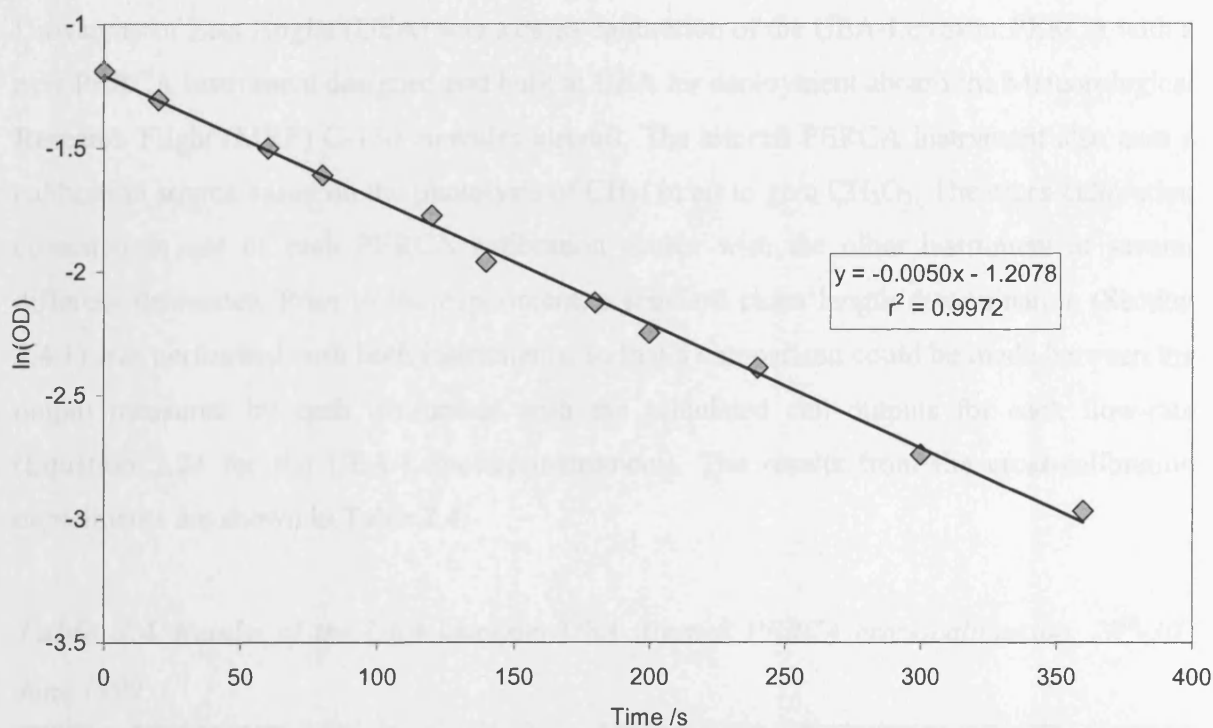


Table 2.3 Results of $j(\text{CH}_3\text{I})$ experiments, June 1999 and February 2001

Cell	$j(\text{CH}_3\text{I})$ measurements / $\times 10^{-3} \text{ s}^{-1}$					Mean ^a
Field cell (June 1999)	5.3	6.5	6.4	5.8	5.1	5.5 (0.2)
	5.7	4.8	5.0	5.1	5.7	
	5.2	5.9	4.9			
Lab cell (Feb. 2001)	5.6	4.1	3.6	7.6	3.8	4.5 (0.4)
	3.0	3.1	5.0	4.9	4.3	
	4.6	4.2				

^a Values in brackets are standard errors on the means.

The mean $j(\text{CH}_3\text{I})$ value obtained for the lab cell ($4.5 \times 10^{-3} \text{ s}^{-1}$), was slightly lower than the mean value originally obtained by *Carpenter* [1996] from experiments carried out in 1994-5 ($5.0 \times 10^{-3} \text{ s}^{-1}$), although the difference was only *ca* 10%. The small observed change was probably due to extensive use of this cell in laboratory experiments at Leicester during 1999 and 2000, and hence slight degradation of the cell mercury lamp output.

In light of these results, the equation for calculating the CH_3O_2 output of the field cell (*cf.* Equation 2.21 for the lab cell, Section 2.4.2) becomes:

$$[\text{CH}_3\text{O}_2] = 5.5 \times 10^{-3} [\text{CH}_3\text{I}] t_{\text{res}} (1 - 0.097 t_{\text{res}} / 2) \quad (2.24)$$

2.4.4 Cross-calibration with the University of East Anglia aircraft PERCA instrument, 28th-30th June 1999

A further collaborative experiment carried out in June 1999 with Dr Tim Green of the University of East Anglia (UEA) was a cross-calibration of the UEA-Leicester PERCA with a new PERCA instrument designed and built at UEA for deployment aboard the Meteorological Research Flight (MRF) C-130 Hercules aircraft. The aircraft PERCA instrument also uses a calibration source based on the photolysis of CH_3I in air to give CH_3O_2 . The cross-calibration consisted in use of each PERCA calibration source with the other instrument at several different flow-rates. Prior to the experiment, a standard chain length determination (Section 2.4.1) was performed with both instruments, so that a comparison could be made between the output measured by each instrument with the calculated cell outputs for each flow-rate (Equation 2.24 for the UEA-Leicester instrument). The results from the cross-calibration experiments are shown in Table 2.4.

Table 2.4 Results of the UEA-Leicester/UEA Aircraft PERCA cross-calibration, 28th-30th June 1999

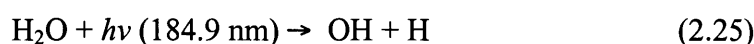
Calibration source	Measured peroxy radical mixing ratios for a given airflow ^a			Mean measured /calculated ratio
	3.0 sLpm	3.5 sLpm	4.0 sLpm	
Leicester-UEA PERCA	68 (59)	42 (50)	34 (45)	0.9
Aircraft PERCA	165 (128)	-	95 (80)	1.2

^aUnits are pptv; values in brackets are calculated peroxy radical mixing ratios based on chain lengths measured prior to the cross-calibration.

The data in Table 2.4 show that the measured and calculated peroxy radical mixing ratios were in reasonable accord for each phase of the experiment, with an average measured/calculated ratio of 1.0 over all five runs. This result gives some confidence that the outputs of the calibration sources are well characterised, and that the PERCA instrument chain lengths in dry air can be determined with reasonable accuracy (see Section 2.4.7).

2.4.5 Cross-calibration with the University of Leeds FAGE HO₂ source, 21st-22nd September 1998

The Leeds FAGE instrument, described briefly in Chapter 1, utilises a calibration system based on the photolysis of water in synthetic air at $\lambda=184.9$ nm, to yield OH, HO₂ and O₃ via the following sequence of reactions:



The mixing ratios of OH and HO₂ generated in the photolysis may then be determined from Equation (2.28):

$$[\text{OH}] = [\text{HO}_2] = \frac{[\text{O}_3][\text{H}_2\text{O}]\sigma_{184.9\text{nm}(\text{H}_2\text{O})\phi_{\text{HO}_x}}{[\text{O}_2]\sigma_{184.9\text{nm}(\text{O}_2)\phi_{\text{O}_3}} \quad (2.28)$$

where σ is the absorption cross-section of water or oxygen at 184.9 nm and ϕ is the photodissociation quantum yield ($\phi_{\text{HO}_x} = \phi_{\text{OH}} = \phi_{\text{HO}_2} = 1$; $\phi_{\text{O}_3} = 2$). The photolysis occurs *ca* 2.5 cm from the end of a 1 m long quartz flow tube of internal diameter 22 mm. A fraction of the flow is sampled (in this case in the PERCA inlet), whilst the remainder is sampled by both ozone (UV; Enviro Technology 400) and water (IR; ADC 700) analysers. Different mixing ratios of ozone and HO_x are obtained in the flow-tube by varying the proportion of synthetic air passing through a deionised water bubbler prior to photolysis. For further details of the Leeds FAGE instrument calibration system, see *Creasey et al.* [1997].

A cross-calibration experiment using the FAGE calibration source with the PERCA instrument was carried out in this laboratory in September 1998 in collaboration with Dr James Lee of the University of Leeds. For the purposes of this cross-calibration, it may be

noted that the mixing ratios of OH and HO₂ produced by the FAGE calibration source during each phase of the experiment were equal; both species were detectable by the PERCA instrument, since OH reacts with CO in the inlet to yield HO₂ (reactions 2.2 and 2.3; see Section 2.1):



Three separate experiments were carried out, at total flow-rates of 8, 9 and 12 sLpm, varying the flow rate through the water bubbler between 0 and 9 sLpm in each case. Each flow rate was maintained for *ca* 10 min, and the average ΔNO₂ signal obtained for each phase of the experiment was calculated. The raw data obtained from all three experiments are plotted on the same axes in Figure 2.10. Qualitatively, Fig. 2.10 shows that the PERCA response was lower in the third experiment, where the total flow-rates were higher, and consequently [HO₂+OH] was significantly lower. In each run, the PERCA response with increasing [H₂O] (and hence [HO₂+OH]) was strongly non-linear, suggestive of a decrease in chain length with increasing [H₂O]. Using the [HO₂] values pertaining to the conditions used supplied by Dr James Lee after the experiment, PERCA chain lengths could be derived for all three experiments (Figure 2.11), assuming that the quantity measured by the PERCA instrument was actually [HO₂+OH] (and recalling that [HO₂] = [OH]; Equation 2.28). The data in Fig. 2.11 indicate that the PERCA chain length did indeed decline in each experiment with increasing [H₂O], although the chain lengths implied by these measurements at low [H₂O] (200-300) seem anomalously high. (Typical CLN values in the course of this project derived from CH₃O₂ calibrations were of the order 40-80, although higher values, up to a maximum of about 200, have been previously observed with the UEA-Leicester instrument.) In addition, no account is taken here of the fact that the PERCA HO₂ detection efficiency was found by *Ashbourn et al.* [1998] to be 69%, which would further increase the observed CLN values in this experiment by *ca* 15%, assuming quantitative detection of OH. Further PERCA-FAGE cross-calibration experiments to clarify these issues are planned at the time of writing.

Figure 2.10 Raw data obtained in the PERCA cross-calibration experiment using the FAGE HO_2/OH source, 21st-22nd September 1998

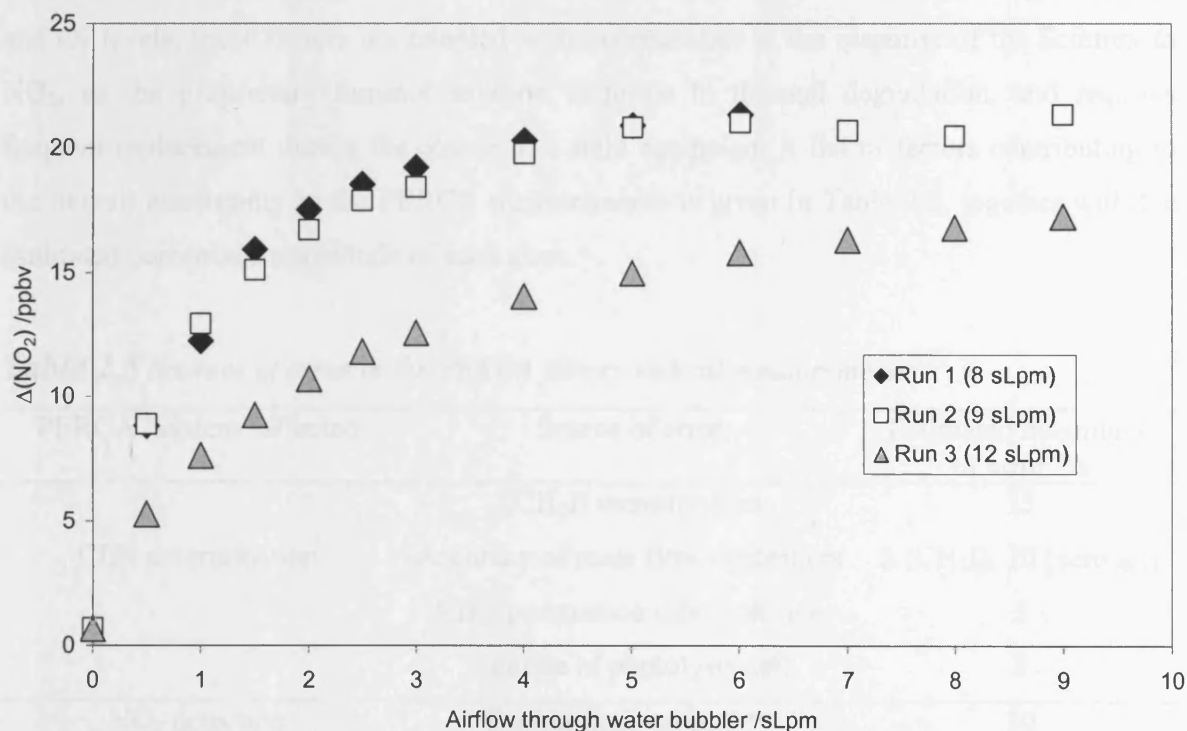
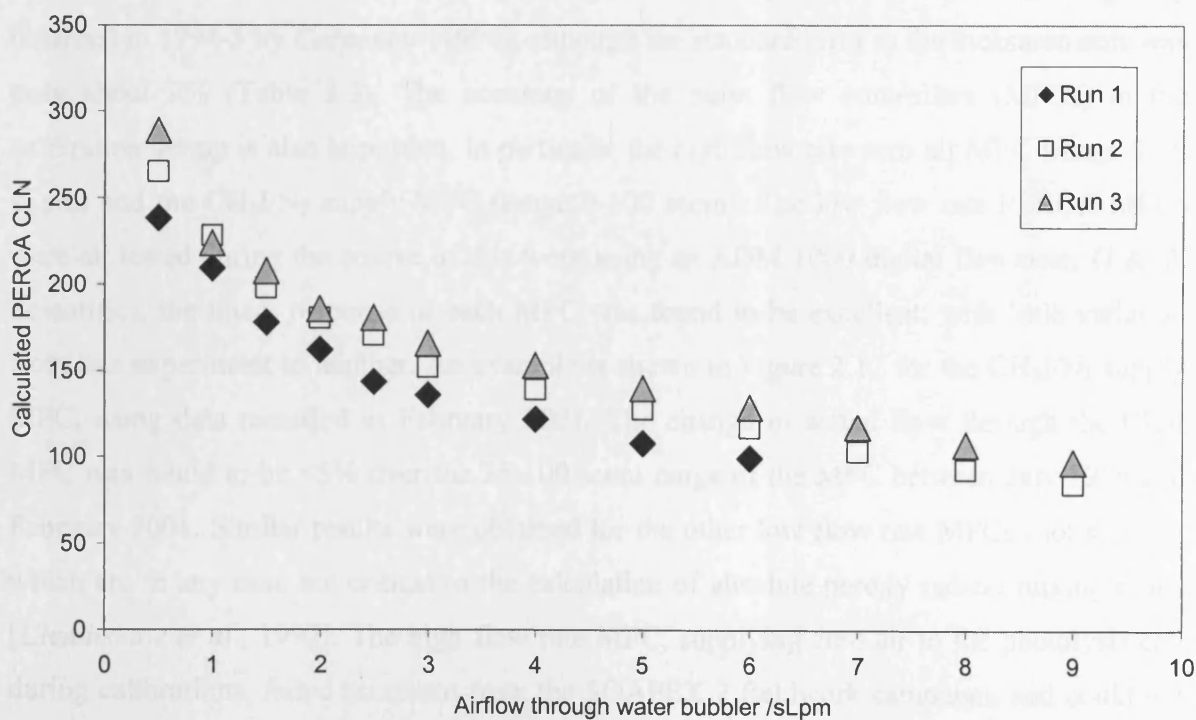


Figure 2.11 Dependence of PERCA CLN with $[\text{H}_2\text{O}]$ in the FAGE cross-calibration experiment, 21st-22nd September 1998



2.5 Discussion of Uncertainties in the PERCA Measurements

The major sources of error in the PERCA peroxy radical measurements are the peroxy radical calibrations (*i.e.*, chain length determinations) and the variability of ambient background NO₂ and O₃ levels; these factors are coupled with uncertainties in the response of the Scintrex to NO₂, as the proprietary luminol solution is prone to thermal degradation, and requires frequent replacement during the course of a field campaign. A list of factors contributing to the overall uncertainty in the PERCA measurements is given in Table 2.5, together with the estimated percentage magnitude of each error.

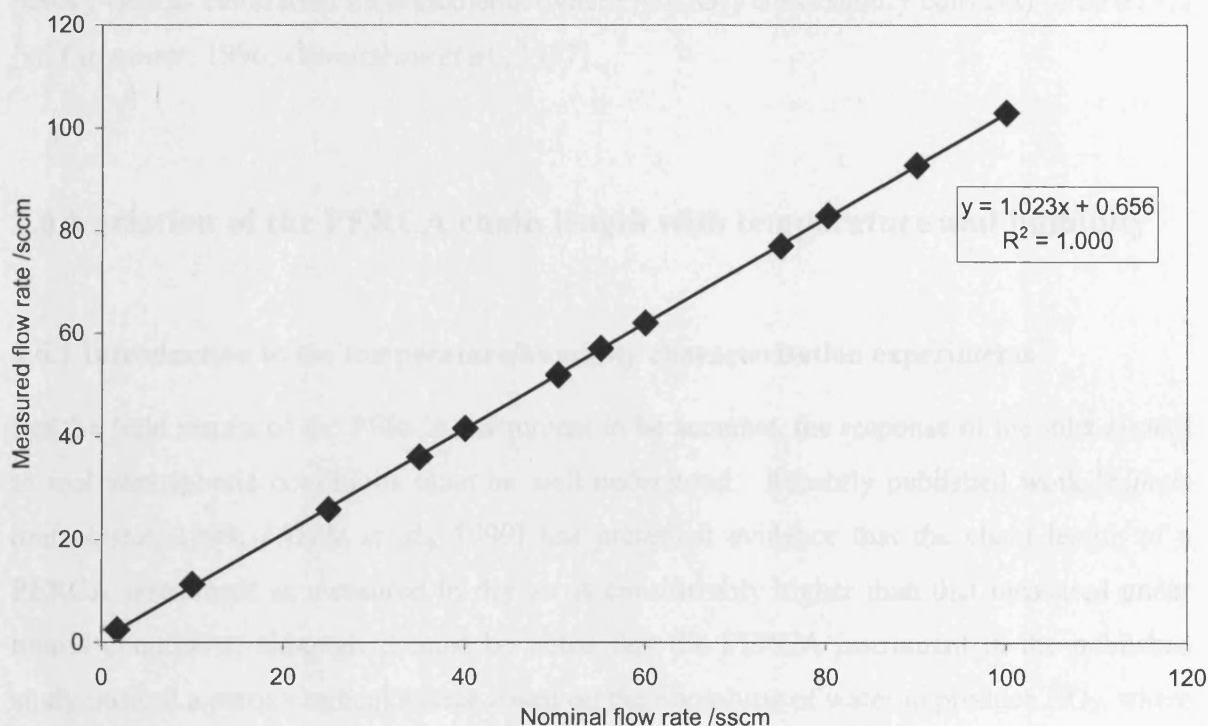
Table 2.5 Sources of error in the PERCA peroxy radical measurements

PERCA 'system' affected	Source of error	Estimated magnitude of error /%
	$j(\text{CH}_3\text{I})$ measurement	15
CLN determination	Accuracy of mass flow controllers	5 (CH ₃ I); 10 (zero air)
	CH ₃ I permeation tube leak rate	5
	Volume of photolysis cell	5
NO ₂ detection	Background variability	20
	Thermal instability of luminol	20

The total error in the radical calibration comprises several factors. These include the uncertainty in the determination of $j(\text{CH}_3\text{I})$ (Section 2.4.3), which is taken to be $\pm 15\%$, since the recently measured value for the lab cell was $4.5 \times 10^{-3} \text{ s}^{-1}$, some 10% lower than originally obtained in 1994-5 by *Carpenter* [1996], although the standard error in the measurements was only about 9% (Table 2.3). The accuracy of the mass flow controllers (MFCs) in the calibration set-up is also important, in particular the high flow rate zero air MFC (range 0-10 sLpm) and the CH₃I/N₂ supply MFC (range 0-100 sccm). The low flow rate PERCA MFCs were all tested during the course of this work using an ADM 1000 digital flowmeter (J & W Scientific); the linear response of each MFC was found to be excellent, with little variation from one experiment to another. An example is shown in Figure 2.12 for the CH₃I/N₂ supply MFC, using data recorded in February 2001. The change in actual flow through the CH₃I MFC was found to be <5% over the 25-100 sccm range of the MFC between July 1999 and February 2001. Similar results were obtained for the other low flow rate MFCs (not shown), which are in any case not critical to the calculation of absolute peroxy radical mixing ratios [*Clemmitshaw et al.*, 1997]. The high flow rate MFC, supplying zero air to the photolysis cell during calibrations, failed on return from the SOAPEX 2 fieldwork campaign, and could not

therefore be calibrated. The unit was instead returned to Millipore for service and recalibration; on return from Millipore the MFC was guaranteed to within 1% of nominal flow at 50% (5 sLpm) and 100% (10 sLpm) flow rate. Nevertheless, a $\pm 10\%$ uncertainty in the zero air flow-rate has been assumed for the purposes of overall PERCA uncertainty estimation, given the lack of an absolute calibration for previous field campaigns [cf. Carpenter, 1996].

Figure 2.12 Nominal and measured N_2 flow rates through the CH_3I MFC, 21st February 2001



The leak rate of the CH_3I permeation tube was found to be quite stable in the period 1998-2001, with a mean value of 197 ng min^{-1} , and a range of *ca* $190\text{--}210 \text{ ng min}^{-1}$, or about $\pm 5\%$. The percentage error over the period of a field campaign (typically six weeks or so) is likely to be even smaller. Similarly, the uncertainty in the measurement of the photolysis cell volume is estimated to be small (5%). The overall uncertainty in the chain length determinations based on these contributory, independent errors (Table 2.5) is estimated to be $\sqrt{\{(0.15)^2 + (0.10)^2 + 3(0.05)^2\}} = 0.2$ or $\pm 20\%$.

The uncertainties in the PERCA measurements arising from background variability in $[NO_2 + O_3]$ and changes in the response of the luminol solution during the course of a field campaign (and hence error in the measured ΔNO_2 values each minute) are more difficult to

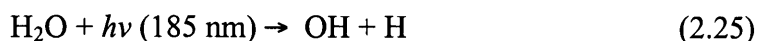
quantify. *Carpenter* [1996] originally estimated a total uncertainty from these effects of $\pm 20\%$. If the two contributions are treated independently, with a reasonable estimated error of $\pm 20\%$ from each, as shown in Table 2.5, their combined contribution is *ca* $\pm 28\%$, which gives an overall PERCA uncertainty of $\sqrt{\{(0.20)^2 + (0.28)^2\}} = 0.35$ or $\pm 35\%$, slightly more than the original published value of $\pm 30\%$ [*Carpenter*, 1996; *Clemmitshaw et al.*, 1997]. This estimate takes no account of the effect of humidity in the PERCA inlet, which is considered in Section 2.6 and Chapter 6.

The precision of the PERCA measurements was estimated from the standard deviation of peroxy radical calibration measurements (where $[\text{CH}_3\text{O}_2]$ is essentially constant) to be $\pm 15\%$ [*cf. Carpenter*, 1996; *Clemmitshaw et al.*, 1997].

2.6 Variation of the PERCA chain length with temperature and humidity

2.6.1 Introduction to the temperature/humidity characterisation experiments

For the field results of the PERCA instrument to be accurate, the response of the inlet system to real atmospheric conditions must be well understood. Recently published work [*Mihele and Hastie*, 1998; *Mihele et al.*, 1999] has presented evidence that the chain length of a PERCA instrument as measured in dry air is considerably higher than that measured under humid conditions, although it must be noted that the PERCA instrument in the published study utilised a peroxy radical source based on the photolysis of water to produce HO_2 , where sufficient CO was added to ensure conversion of OH to HO_2 (several 100 ppmv) [*Schultz et al.*, 1995]:



Since calibrations are performed using a dry gas stream, it was essential to verify and quantify this effect for the UEA-Leicester instrument. In addition, the effects of varying the temperature of the inlet must be considered. The UEA-Leicester PERCA instrument has been run with the inlet heated above ambient temperature (*ca* 300 K) in all field campaigns since 1996 (including all three campaigns considered in this thesis) in an effort to reduce the

discrepancy between 'dry' and 'wet' chain lengths; before now no laboratory work has been carried out to determine the effectiveness of this refinement to the instrument.

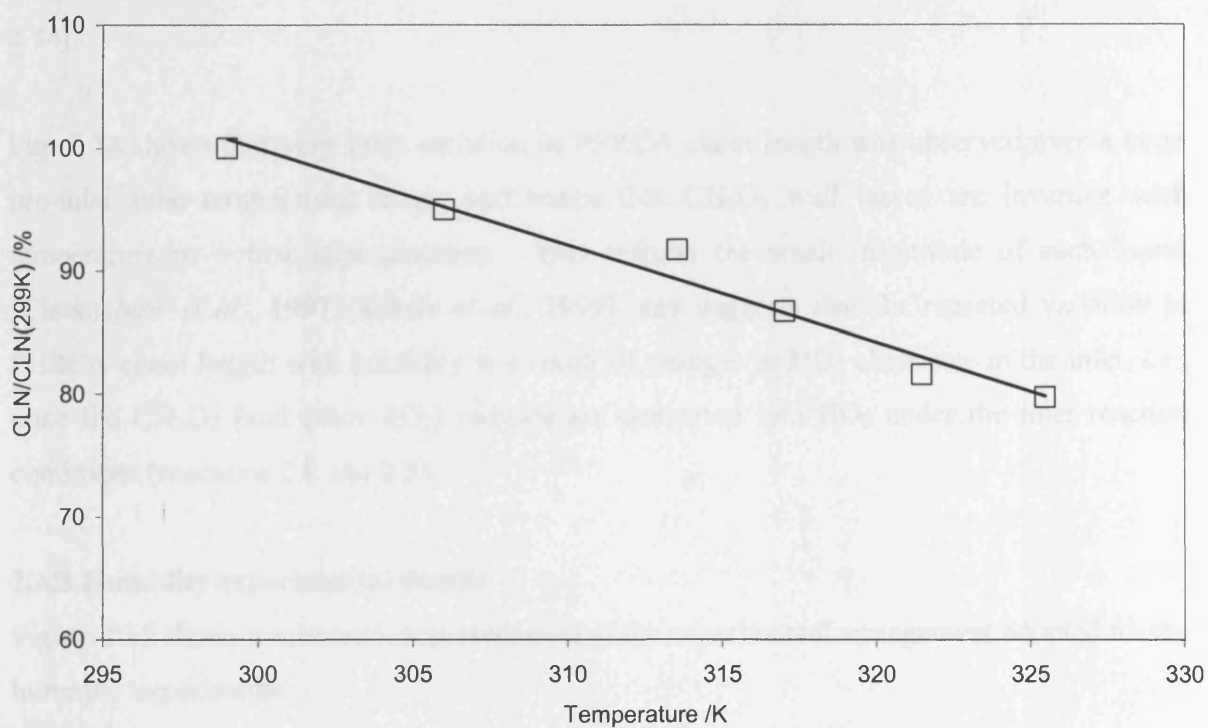
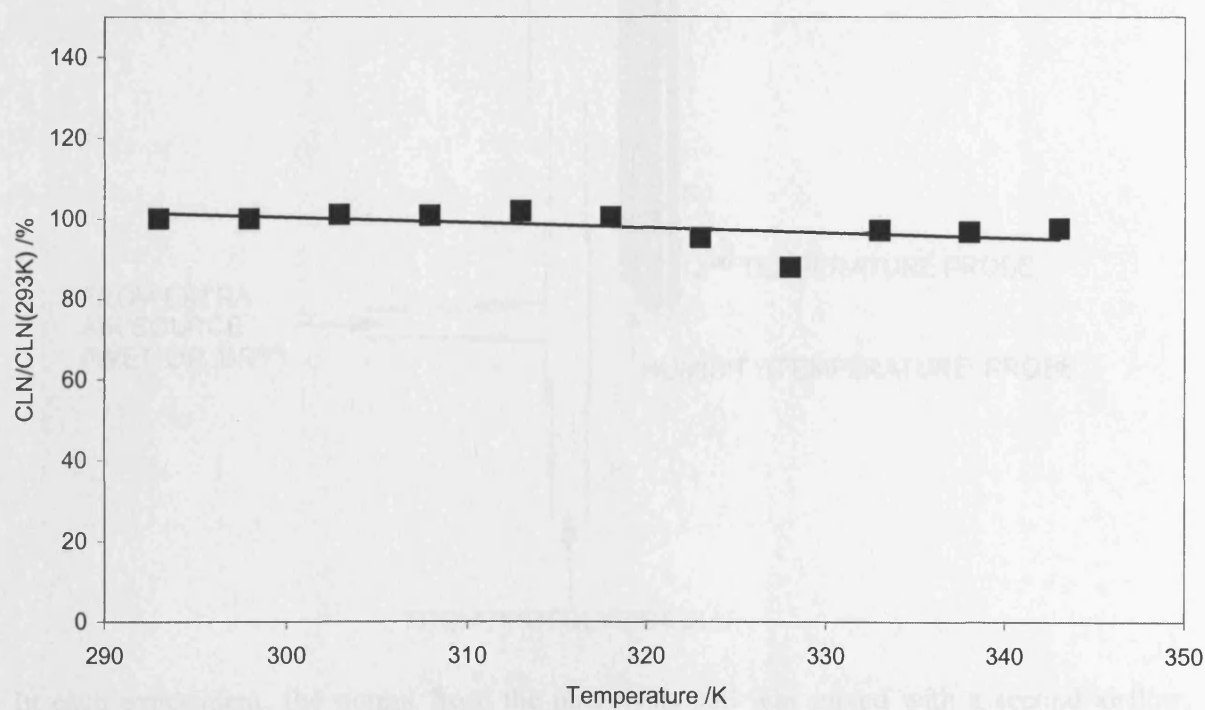
An additional complication is that humidity in the inlet might affect either wall losses of peroxy radicals and/or the inlet chemistry itself. In order to distinguish between these two possibilities it has proved useful to carry out laboratory characterisation experiments employing an additional glass tube fitted with a condenser jacket inserted between the output of the calibration source and the PERCA inlet (referred to below as the *pre-inlet tube*). In this way, temperature and humidity effects on the chain length could be investigated both in the inlet alone and in the pre-inlet tube combined with the inlet system.

This section presents the results of a series of experiments to look at the response of the UEA-Leicester PERCA instrument to varying specific humidity and inlet temperature carried out between August 1998 and October 2000. First, the dependence of the PERCA chain length (CLN) with varying temperature under dry conditions is investigated. Second, the effect on the PERCA CLN of varying the 'ambient' humidity at standard operating temperatures (25-30°C) is considered. Finally, the results of an extensive series of experiments where both temperature and humidity were varied in the PERCA inlet are presented. These results are compared with some simple modelling studies of the PERCA inlet chemistry using the FACSIMILE for Windows package (Version 1.0; *AEA Technology*, 1995; see Section 2.6.6 for more details).

2.6.2 Dependence of the PERCA chain length on temperature in dry air

Throughout this set of experiments, and those described in the following sections, the PERCA inlet temperature was varied using a specially made glass inlet fitted with a condenser jacket, through which water at temperatures in the range 278-333 K could be pumped from a circulating bath. The temperature inside the inlet was monitored using a Testo 501 thermocouple (Testo Ltd), comprising a 3 mm diameter, 200 mm long probe, which could be inserted into the middle of the inlet.

Figure 2.13 shows the results of two experiments to examine the variation of chain length with varying inlet temperature (*i.e.*, no pre-inlet tube employed), where chain length measurements are expressed as a percentage of the value obtained for a temperature of 299 K. Fig. 2.13 indicates that a small, but consistent decrease in chain length was observed with

Figure 2.13 Dependence of PERCA chain length on inlet temperature in dry air**Figure 2.14** Dependence of PERCA chain length with varying pre-inlet tube temperature (inlet temperature ca 296 K)

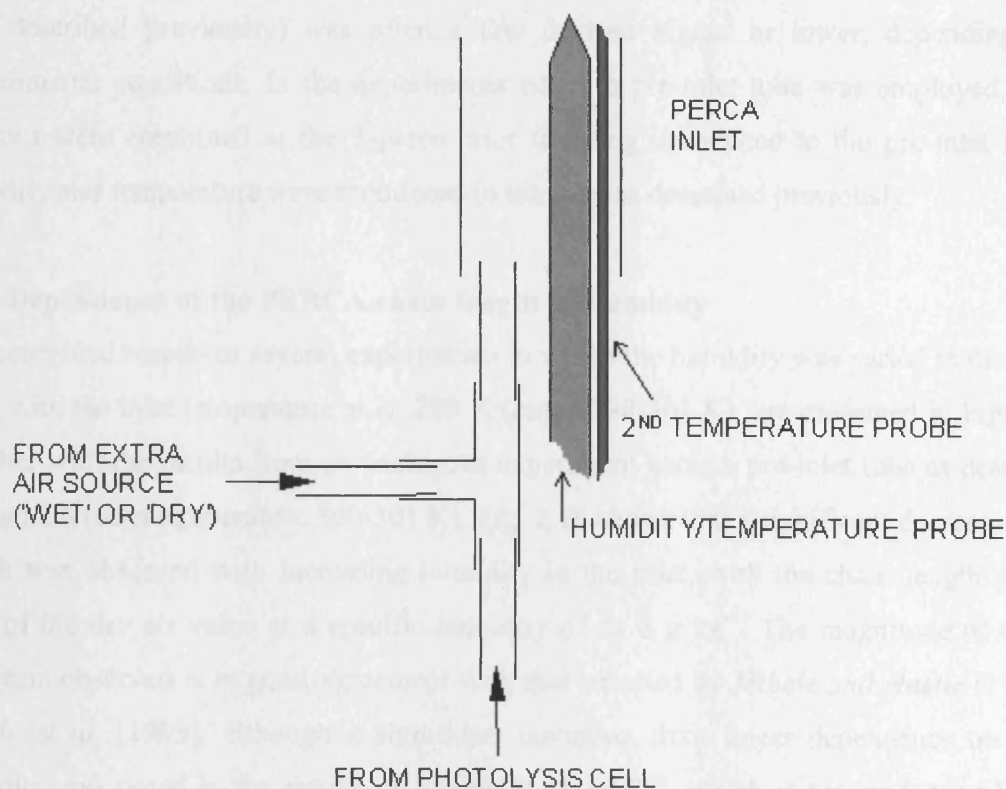
increasing temperature. Further experiments were carried out maintaining the inlet temperature at *ca* 296 K, whilst varying the temperature of the pre-inlet glass tube (see Figure 2.14).

Fig. 2.14 shows that very little variation in PERCA chain length was observed over a large pre-inlet tube temperature range, and hence that CH_3O_2 wall losses are invariant with temperature to a first approximation. This reflects the small magnitude of such losses [Clemmitshaw *et al.*, 1997; Mihele *et al.*, 1999], and suggests that the reported variation in PERCA chain length with humidity is a result of changes in HO_2 chemistry in the inlet, *i.e.*, once the CH_3O_2 (and other RO_2) radicals are converted into HO_2 under the inlet reaction conditions (reactions 2.4 and 2.5).

2.6.3 Humidity experimental details

Figure 2.15 shows a schematic representation of the experimental arrangement adopted for the humidity experiments.

Figure 2.15 Apparatus used in the PERCA humidity experiments



In each experiment, the output from the photolysis cell was mixed with a second airflow, which was either passed directly from a 2.5 sLpm GPV212 flow meter (Platon Flowbits) to

the T-piece shown in Fig. 2.15, or indirectly *via* two Dreschel bottles containing deionised water. By varying the flow rates through the photolysis cell and through the second supply line, varying humidity levels could be achieved in the inlet. In order to be certain that a change in CLN could be attributed to humidity, and not to a change in total airflow or some other variable, each combination of flow rates was repeated for both ‘dry’ and ‘wet’ conditions, *i.e.*, with the second airflow passing directly into the inlet and *via* the water bubblers. The ratio of observed chain lengths in the two runs (wet/dry) was then calculated. This procedure also obviated the need for a constant chain length in dry conditions, allowing results to be compared from experiments widely separated in time. The relative humidity in the inlet (RH) was measured using an M1 hygrometer (Rotronic), the end of which was positioned to be just below the top of the Teflon tube carrying CH_3O_2 radicals into the inlet, in order to avoid excessive radical losses on the metal surface of the probe. Since the temperature was also measured by the hygrometer, the RH values could be converted to specific humidity, defined as the mass of water *per* mass of moist air (typically measured in g kg^{-1}); this is a more useful measure of the water vapour content of air than relative humidity, as it is independent of temperature (see Appendix for details). The same specific humidity was then assumed to be present in the reaction zone of the inlet (between addition points **A** and **B** in Fig. 2.2), where the temperature (measured using the Testo 501 thermocouple (Testo Ltd) described previously) was often a few degrees higher or lower, depending on the experimental conditions. In the experiments where a pre-inlet tube was employed, the two airflows were combined at the T-piece prior to being introduced to the pre-inlet tube; the humidity and temperature were monitored in the inlet as described previously.

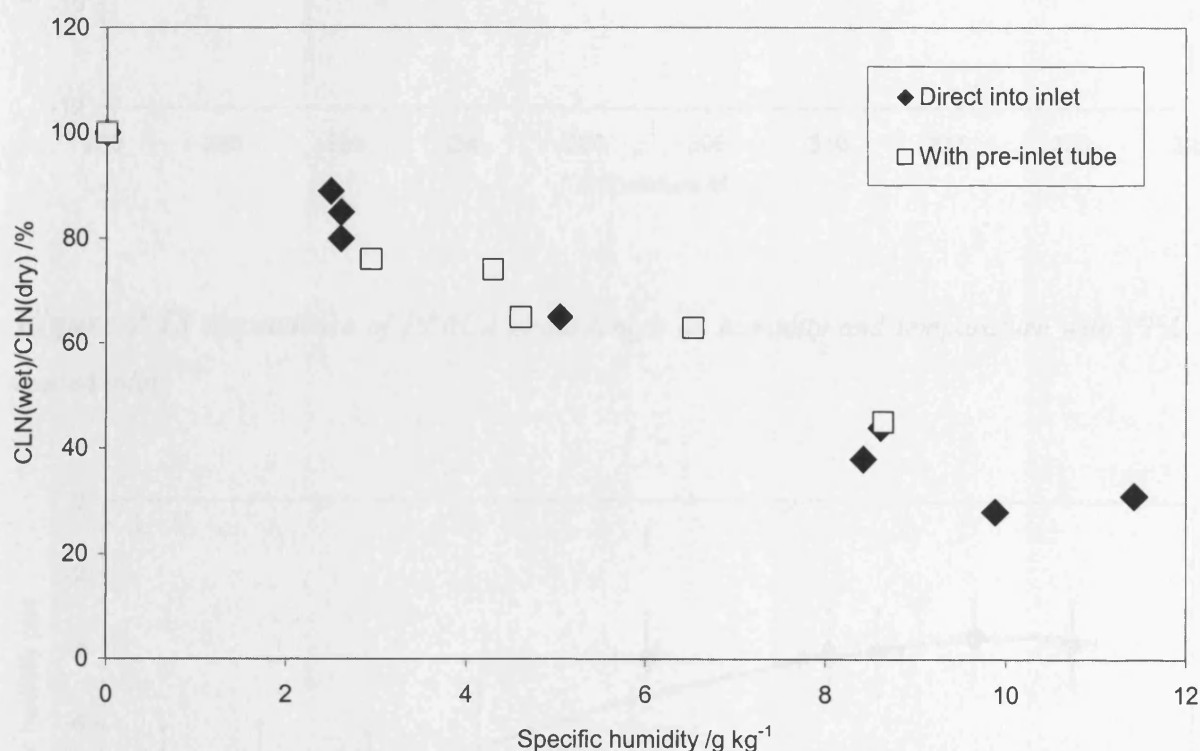
2.6.4 Dependence of the PERCA chain length on humidity

The combined results of several experiments in which the humidity was varied in the PERCA inlet, with the inlet temperature at *ca* 299 K (range 298-301 K), are presented in Figure 2.16, together with the results from an analogous experiment using a pre-inlet tube as described in Section 2.6 (inlet temperature 300-301 K). Fig. 2.16 shows that a significant decrease in chain length was observed with increasing humidity in the inlet, with the chain length falling to 50% of the dry air value at a specific humidity of *ca* 8 g kg^{-1} . The magnitude of the CLN reduction observed is in good agreement with that reported by *Mihele and Hastie* [1998] and *Mihele et al.* [1999], although a significant deviation from linear dependence on specific humidity was noted in the results of *Mihele et al.* [1999], which is not evident in Fig. 2.16 (see also the cross-calibration with the Leeds-FAGE OH/HO₂ source in Section 2.4.5). This difference may be due to the interaction of two effects: CLN reduction in humid air, coupled

with the reported slightly increased efficiency of HO_2 detection in humid air compared with dry air [Ashbourn *et al.*, 1998].

Although there was a slight difference in mean temperature between the inlet and pre-inlet tube experiments, Fig. 2.16 also shows that there was no significant difference between the trends observed under the two sets of conditions. This result suggests once again that wall losses of CH_3O_2 radicals are not a particularly important factor in the response of the PERCA technique to water vapour in the inlet.

Figure 2.16 Variation of PERCA chain length with humidity at an inlet temperature of 25–28 °C



2.6.5 Dependence of the PERCA chain length on humidity and temperature

Further experiments were carried out in order to investigate the influence of changing inlet temperature on the CLN-humidity effect. Since the response of the chain length to humidity was generally well described by a straight line at a given temperature (Fig. 2.16), it proved possible to plot the gradient of the trend lines obtained for each experiment against temperature (Figure 2.17). Some variation in the inlet temperature was generally observed in the course of an experiment; for this reason, error bars are shown for the abscissa as well as the ordinate in Fig. 2.17 to give an indication of the temperature range recorded in each case

Figure 2.17 Dependence of PERCA chain length on humidity and temperature

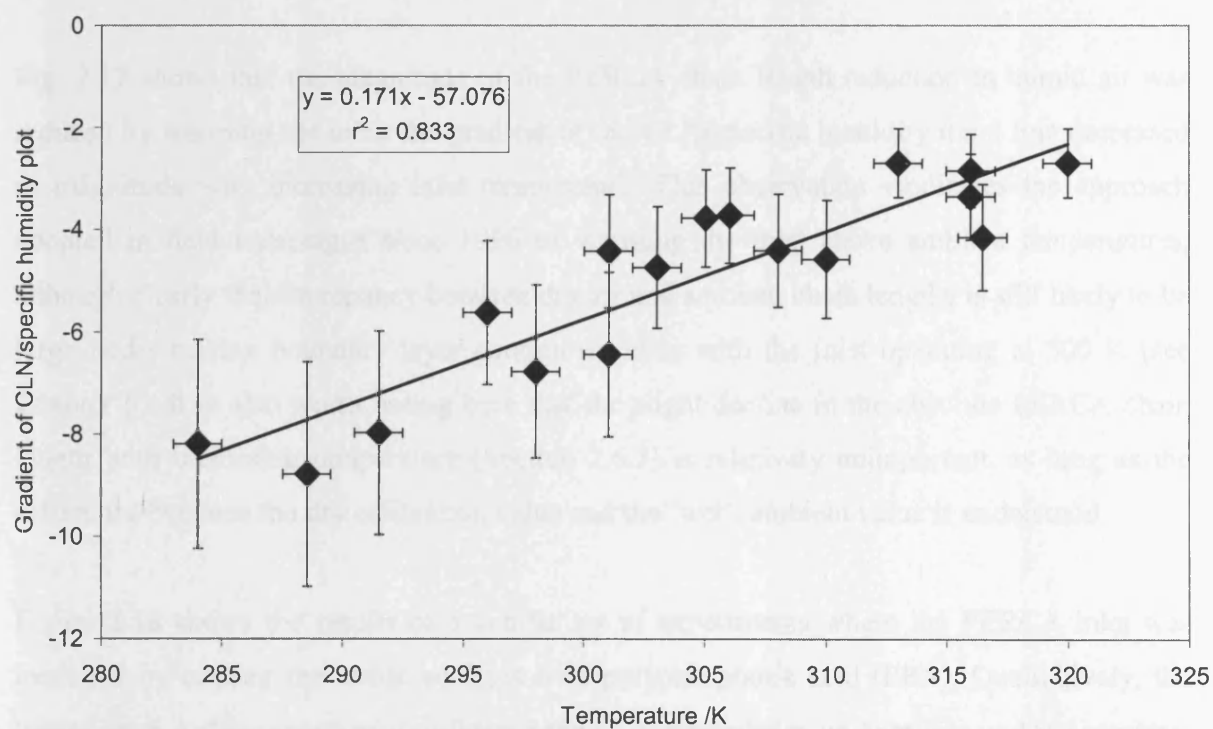
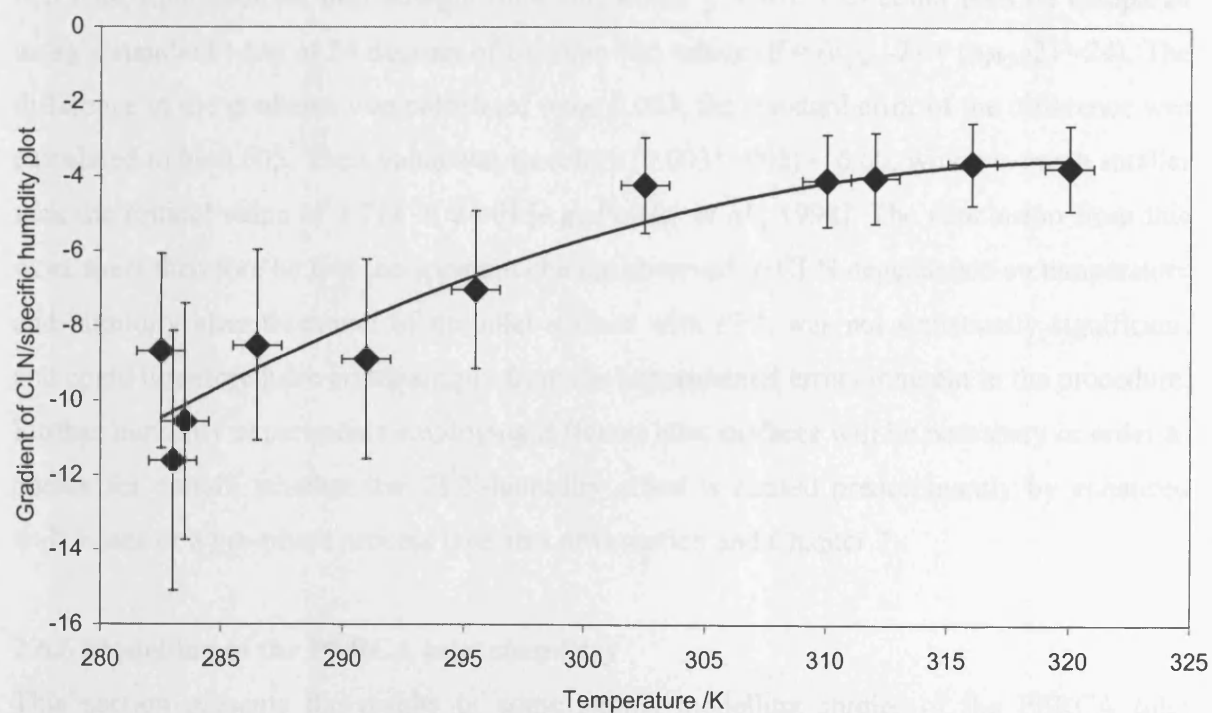


Figure 2.18 Dependence of PERCA chain length on humidity and temperature with PPA-coated inlet



(typically ± 1 K). The ordinate error bars ($\pm 25\%$) are based on linear regression analyses of individual experiments, which typically gave a standard error in the gradient of *ca* 20-25%.

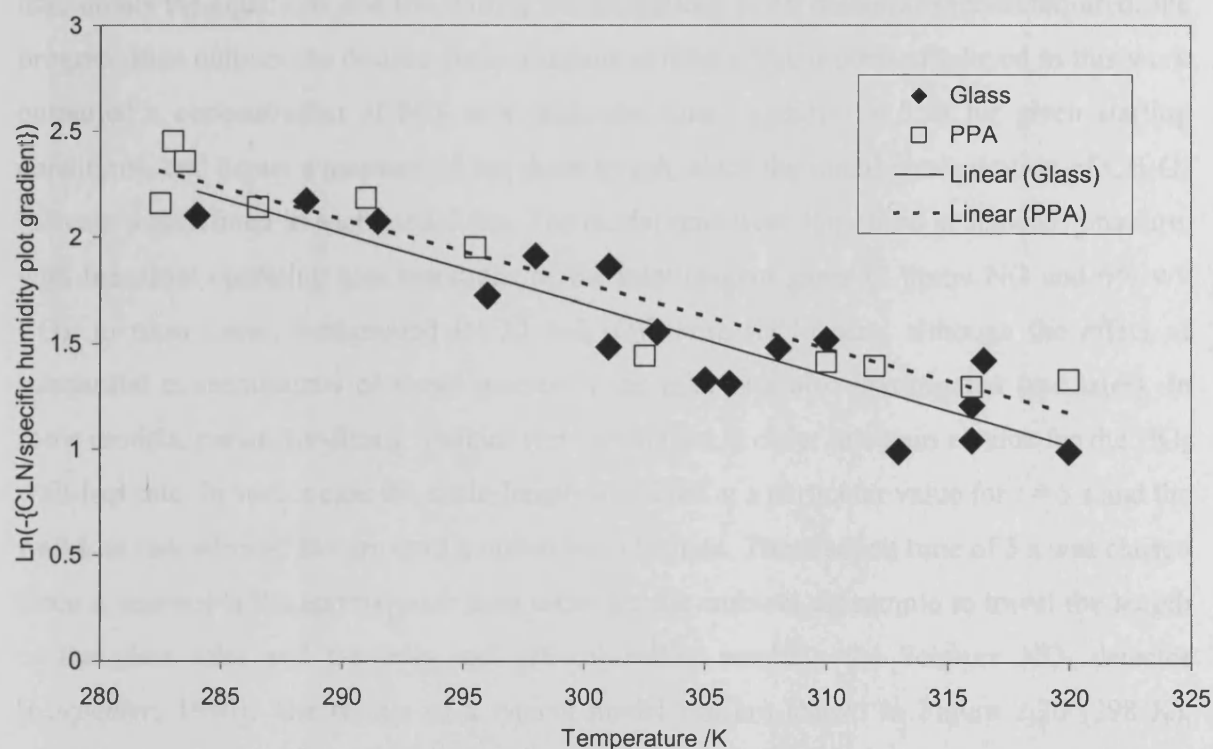
Fig. 2.17 shows that the magnitude of the PERCA chain length reduction in humid air was reduced by warming the inlet: the gradient of the CLN/specific humidity trend line decreased in magnitude with increasing inlet temperature. This observation vindicates the approach adopted in field campaigns since 1996 of warming the inlet above ambient temperatures, although clearly the discrepancy between dry air and ambient chain lengths is still likely to be large under marine boundary layer conditions, even with the inlet operating at 300 K (see Chapter 6). It is also worth noting here that the slight decline in the absolute PERCA chain length with increasing temperature (Section 2.6.3) is relatively unimportant, as long as the difference between the dry calibration value and the 'wet', ambient value is understood.

Figure 2.18 shows the results of a similar set of experiments where the PERCA inlet was modified by coating the inside surfaces with polyphosphoric acid (PPA). Qualitatively, the treated inlet surface appeared to influence the CLN dependence on humidity and temperature, with slightly steeper gradients observed at the low end of the temperature range, but little dependence on temperature noted above *ca* 300 K. In order to see if this apparent difference was statistically significant, both data sets (Figs 2.17 and 2.18) were natural-log ($\ln$) transformed in order to obtain two reasonable straight lines (Figure 2.19). The gradients of the two least-squares-fitted best straight lines (m ; where $y = mx + c$) could then be compared using a standard t-test at 24 degrees of freedom (df ; where $df = (n_{\text{glass}} - 2) + (n_{\text{PPA}} - 2) = 24$). The difference in the gradients was calculated to be 0.003; the standard error of the difference was calculated to be 0.005. The t value was therefore $(0.003/0.005) = 0.60$, which is much smaller than the critical value of 1.711 at 24 df [*e.g.*, Fowler *et al.*, 1998]. The conclusion from this work must therefore be that the apparent change observed in CLN dependence on temperature and humidity after treatment of the inlet surface with PPA was not statistically significant, and could therefore have arisen simply from the experimental errors inherent in the procedure. Further humidity experiments employing different inlet surfaces will be necessary in order to decide for certain whether the CLN-humidity effect is caused predominantly by enhanced wall losses or a gas-phase process (see also next section and Chapter 7).

2.6.6 Modelling of the PERCA inlet chemistry

This section presents the results of some simple modelling studies of the PERCA inlet chemistry using the FACSIMILE for Windows package (Version 1.0; AEA Technology,

Figure 2.19 Comparison of PERCA CLN-humidity dependence for glass and PPA-covered inlet surface



1995); Table 2.6 shows the suite of reactions used in the models [Carpenter, 1996; Clemitshaw *et al.*, 1997]. The rate coefficients for all reactions were taken from DeMore *et al.*

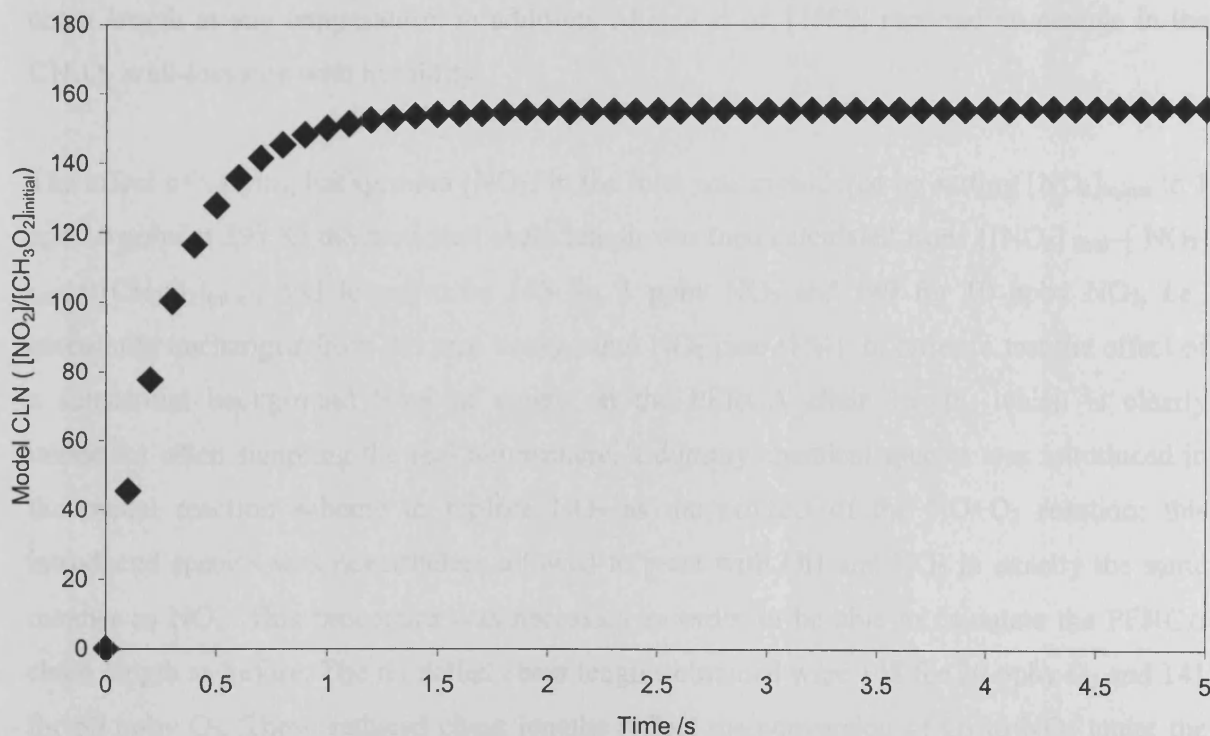
Table 2.6 Reaction scheme used in FACSIMILE modelling of PERCA inlet chemistry

Reaction	Rate expression /cm ³ molecule ⁻¹ s ⁻¹ except [†] s ⁻¹
HO ₂ + NO → OH + NO ₂	3.7E-12*EXP(250/T)
OH + CO → HO ₂ + CO ₂	1.5E-13*(1+0.6*Pressure)
OH + NO + M → HONO + M	Troe expression ^a
OH + NO ₂ + M → HONO ₂ + M	Troe expression ^a
OH + HONO → H ₂ O + NO ₂	1.8E-11*EXP(-390/T)
HO ₂ + NO ₂ + M → HO ₂ NO ₂ + M	Troe expression ^a
OH + H ₂ O ₂ → HO ₂ + H ₂ O	2.9E-12*EXP(-160/T)
HO ₂ + OH → H ₂ O + O ₂	4.8E-11*EXP(250/T)
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	{(2.3E-13*EXP(600/T) + (1.7E-33*M*EXP(1000/T)) *(1+1.4E-21*H ₂ O*EXP(2200/T))}
OH + O ₃ → HO ₂ + O ₂	1.6E-12*EXP(-940/T)
HO ₂ + O ₃ → OH + 2O ₂	1.1E-14*EXP(-500/T)
NO + O ₃ → NO ₂ + O ₂	2.0E-12*EXP(-1400/T)
HO ₂ + CH ₃ O ₂ → CH ₃ O ₂ H + O ₂	3.8E-13*EXP(800/T)
CH ₃ O ₂ + NO → CH ₃ O + NO ₂	4.2E-12*EXP(180/T)
CH ₃ O + O ₂ → HCHO + HO ₂	3.9E-14*EXP(-900/T)
CH ₃ O + NO + M → CH ₃ ONO + M	Troe expression ^a
HO ₂ NO ₂ → HO ₂ + NO ₂	8.62E-2 ^{†b}
HO ₂ + walls → products	2.8 [Mihele <i>et al.</i> , 1999] or parameterised (see text) [†]

^aTermolecular rate coefficients were converted into bimolecular rate coefficients $k(M,T)$ using the Troe expression recommended by DeMore *et al.* [1997]. ^b Atkinson [1997].

[1997], unless otherwise stated. The FACSIMILE program is essentially a routine for solving sets of ordinary differential equations by an iterative method over a specified time period. The user inputs the equations and the starting concentrations of all chemical species required; the program then outputs the desired concentrations at time t . The models employed in this work outputted a concentration of NO_2 at a particular time (usually $t = 5$ s) for given starting conditions, and hence a measure of the chain length, since the initial concentration of CH_3O_2 radicals was defined in each model run. The model runs were initialised at standard pressure, with the usual operating concentrations of the inlet reagent gases (3 ppmv NO and 6% v/v CO). In most cases, background $[\text{NO}_2]$ and $[\text{O}_3]$ were set to zero, although the effect of substantial concentrations of these species in the inlet was also investigated (see later). In some models, parameter-fitting routines were employed in order to obtain a value for the HO_2 wall-loss rate. In such a case the chain length was fixed at a particular value for $t = 5$ s and the wall-loss rate allowed to vary until a match was obtained. The reaction time of 5 s was chosen since it represents the approximate time taken for the ambient air sample to travel the length of the glass inlet and the inlet reel (16 m) before reaching the Scintrex NO_2 detector [Carpenter, 1996]. The results of a typical model run are shown in Figure 2.20 (298 K), where background $[\text{NO}_2]$ and $[\text{O}_3]$ were set to zero, and the model CLN at $t = 5$ s was 154.

Figure 2.20 Modelled PERCA chain length at 298 K



A sensitivity analysis of the inlet chemistry scheme shown in Table 2.6 was performed by varying each rate coefficient in turn by $\pm 25\%$ (with zero background $[\text{O}_3]$ and $[\text{NO}_2]$). The only reactions for which such a change resulted in more than a 5% change in the modelled chain length value were the $\text{HO}_2 + \text{NO}$ reaction (2.1), the $\text{OH} + \text{CO}$ reaction (2.2), the $\text{OH} + \text{NO}$ reaction (2.9) and the HO_2 wall-loss reaction (2.10). Unsurprisingly, increasing the rates of the first two of these processes increased the chain length, whilst an increase in the rates of the second pair of reactions resulted in a reduced chain length. The mean absolute changes in modelled chain length for the four indicated reactions were 19%, 6%, 6% and 19%, respectively; these results suggest that the propagation/loss ratio of OH in the inlet is less important than the propagation/loss ratio of HO_2 in limiting the PERCA chain length, as has been previously assumed.

The model scheme in Table 2.6 was also run over a range of temperatures. A slight increase in the PERCA chain length with increasing temperature ($< 2\%$ over temperature range 278–328 K) was observed, but this was assuming the HO_2 wall-loss rate to be invariant with temperature at 2.8 s^{-1} [Mihele *et al.*, 1999]. Since an experimental decrease of CLN with increasing temperature (in dry air) was observed (see Section 2.6.3, Fig. 2.13), it would seem likely that the HO_2 wall-loss rate in fact increases with temperature, which is perhaps not especially surprising. Modelling of the inlet chemistry with and without the reported CH_3O_2 wall-loss reaction rate [0.8 s^{-1} ; Mihele *et al.*, 1999] produced less than 1% difference in the chain length at any temperature; in addition, Mihele *et al.* [1999] reported no change in the CH_3O_2 wall-loss rate with humidity.

The effect of varying background $[\text{NO}_2]$ in the inlet was considered by setting $[\text{NO}_2]_{\text{initial}}$ to 1 and 10 ppbv at 298 K; the modelled chain length was then calculated from $\{[\text{NO}_2]_{\text{final}} - [\text{NO}_2]_{\text{initial}}\} / [\text{CH}_3\text{O}_2]_{\text{initial}}$, and found to be 153 for 1 ppbv NO_2 and 149 for 10 ppbv NO_2 , *i.e.*, essentially unchanged from the zero background NO_2 case (154). In order to test the effect of a substantial background level of ozone on the PERCA chain length, which is clearly important when sampling the real atmosphere, a dummy chemical species was introduced in the model reaction scheme to replace NO_2 as the product of the $\text{NO} + \text{O}_3$ reaction; this introduced species was nevertheless allowed to react with OH and HO_2 in exactly the same manner as NO_2 . This procedure was necessary in order to be able to calculate the PERCA chain length as before. The modelled chain lengths obtained were 148 for 20 ppbv O_3 and 141 for 50 ppbv O_3 . These reduced chain lengths reflect the conversion of O_3 to NO_2 under the reaction conditions of the PERCA inlet (and hence enhanced losses of HO_x through the

OH+NO₂ and HO₂+NO₂ reactions), although the magnitude of the effect is relatively small, even at relatively high [O₃] (<10% at 50 ppbv).

Assuming that the inlet-chemistry reaction scheme presented in Table 2.6 is complete, one might expect that increases in HO₂ wall-loss rates with increasing humidity are responsible for the observed reduction of the PERCA chain length under humid conditions (see Fig. 2.16). To test this theory, the data obtained in the humidity experiments described in Section 2.6.4 were used to model the inlet chemistry under humid conditions. Using the previously modelled chain length for dry conditions at 298 K, plus the observed ratios of wet/dry chain lengths obtained experimentally at similar temperatures (298-301 K; Fig. 2.16), values for the wall-loss rate coefficient of HO₂ ($k_{\text{HO}_2\text{wall}}$) could be derived for varying specific humidity by parameter fitting, as described previously. The results of this work are plotted in Figure 2.21, along with values for $k_{\text{HO}_2\text{wall}}$ measured experimentally by *Mihele et al.* [1999] for comparison purposes.

Figure 2.21 HO₂ wall-loss rate coefficients ($k_{\text{HO}_2\text{wall}}$): comparison between measurements [Mihele et al., 1999] and modelled results (current work)

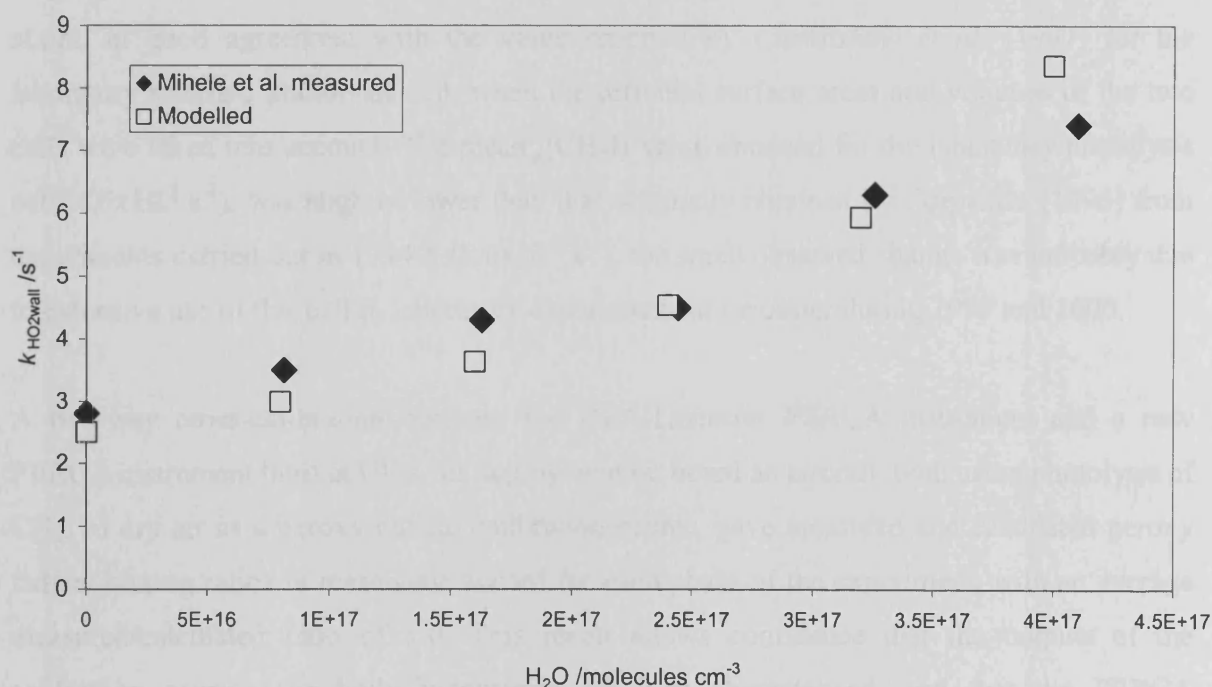
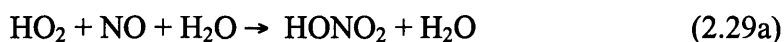


Figure 2.21 shows good agreement between the modelled results and the published experimental results, particularly in the typical ambient humidity range [H₂O] = (2-4) × 10¹⁷ molecules cm⁻³ (specific humidity *ca* 5-10 g kg⁻¹). *Mihele et al.* [1999] postulated an

additional gas-phase reaction for the PERCA inlet chemistry scheme in order to explain their findings:



However, the results presented here suggest that the occurrence of an additional gas-phase reaction is not necessary in order to explain the observed performance of the PERCA instrument in humid conditions. The reduction of chain length can be adequately described by allowing the first-order rate coefficient $k_{\text{HO}_2\text{wall}}$ to vary with specific humidity, as found experimentally by *Mihele et al.* [1999].

2.7 Summary

2.7.1 General summary

Photolysis cell wall-loss experiments carried out using the field calibration cell gave a mean heterogeneous wall-loss rate of $9.7 \pm 1.9\% \text{ s}^{-1}$ for total gas flow-rates of 3.55, 4.55 and 5.55 sLpm, in good agreement with the value reported by *Clemitshaw et al.* [1997] for the laboratory standard photolysis cell, when the different surface areas and volumes of the two cells were taken into account. The mean $j(\text{CH}_3\text{I})$ value obtained for the laboratory photolysis cell ($4.5 \times 10^{-3} \text{ s}^{-1}$), was slightly lower than that originally obtained by *Carpenter* [1996] from experiments carried out in 1994-5 ($5.0 \times 10^{-3} \text{ s}^{-1}$); the small observed change was probably due to extensive use of this cell in laboratory experiments at Leicester during 1999 and 2000.

A two-way cross-calibration between the UEA-Leicester PERCA instrument and a new PERCA instrument built at UEA for deployment on board an aircraft, both using photolysis of CH_3I in dry air as a peroxy radical calibration source, gave measured and calculated peroxy radical mixing ratios in reasonable accord for each phase of the experiment, with an average measured/calculated ratio of 1.0. This result allows confidence that the outputs of the calibration sources for both instruments are well characterised, and that the PERCA instrument chain lengths in dry air can be determined with reasonable accuracy.

A cross-calibration of the PERCA instrument experiment using the FAGE calibration source, based on the photolysis of water to yield HO_2 , showed that the PERCA response declined

non-linearly with increasing $[H_2O]$ (and hence $[HO_2+OH]$), suggestive of a decrease in chain length with increasing $[H_2O]$, although the chain lengths implied by these measurements at low $[H_2O]$ (200-300) seemed anomalously high. Further PERCA-FAGE cross-calibration experiments to clarify these issues are planned at the time of writing.

The systematic uncertainty in the PERCA measurements was estimated to be $\pm 35\%$, slightly more than the original published value of $\pm 30\%$ [Carpenter, 1996; Clemitshaw *et al.*, 1997]; this estimate takes no account of the effect of humidity in the PERCA inlet. The precision of the PERCA measurements was estimated from the standard deviation of peroxy radical calibration measurements (where $[CH_3O_2]$ is essentially constant) to be $\pm 15\%$.

2.7.2 PERCA Instrument Characterisation in Humid Air

Laboratory experiments with the UEA-Leicester PERCA instrument showed that the chain length (CLN) of the inlet amplification reaction decreased markedly with increasing specific humidity, in qualitative agreement with work published by *Mihele and Hastie* [1998] and *Mihele et al.* [1999], who used a peroxy radical source based on the photolysis of water to produce HO_2 (reactions 2.25, 2.2 and 2.3). Although the magnitude of the observed effect was in good agreement with the results of *Mihele et al.* [1999], the dependence of CLN on specific humidity at a given temperature was approximately linear for the UEA-Leicester instrument, whereas a significant deviation from linear dependence on specific humidity was noted in the results of *Mihele et al.* [1999]. This difference may be due to the interaction of two effects when using an HO_2 radical source: CLN reduction in humid air, coupled with the reported slightly increased efficiency of HO_2 detection in humid air compared with dry air [Ashbourn *et al.*, 1998]. A cross-calibration of the UEA-Leicester PERCA instrument with the University of Leeds Fluorescence Assay by Gas Expansion (FAGE) HO_2 source also showed non-linear CLN dependence on humidity in the inlet (Section 2.4).

The addition of the extra, humid airflow into a pre-inlet tube produced an unchanged CLN-humidity effect, which represents evidence that wall losses of CH_3O_2 are not implicated in the PERCA CLN reduction in humid air (Fig. 2.16).

Further experiments were carried out in order to investigate the influence of changing inlet temperature on the CLN-humidity effect: the magnitude of the PERCA chain length reduction in humid air was found to be reduced by warming the inlet; the gradient of the CLN/specific humidity trend line decreased in magnitude with increasing inlet temperature. A qualitatively

different curve was observed in a set of experiments where the glass inlet surface was coated with polyphosphoric acid (PPA), although a standard statistical test showed no significant difference between the two data sets. Further experiments using different inlet surfaces are required in order to be certain that the CLN-humidity effect is due to enhanced HO_2 wall losses in humid conditions. However, modelling of the PERCA inlet chemistry using the measured $\text{CLN}(\text{wet})/\text{CLN}(\text{dry})$ ratios for given temperature and humidity gave fitted HO_2 wall-loss rate coefficients in good agreement with those measured experimentally by *Mihele et al.* [1999], which would suggest that no further gas-phase reaction need be invoked to explain the observed CLN-humidity effect.

Chapter 3 – Night-time Chemistry at Mace Head, Ireland

3.1 Introduction

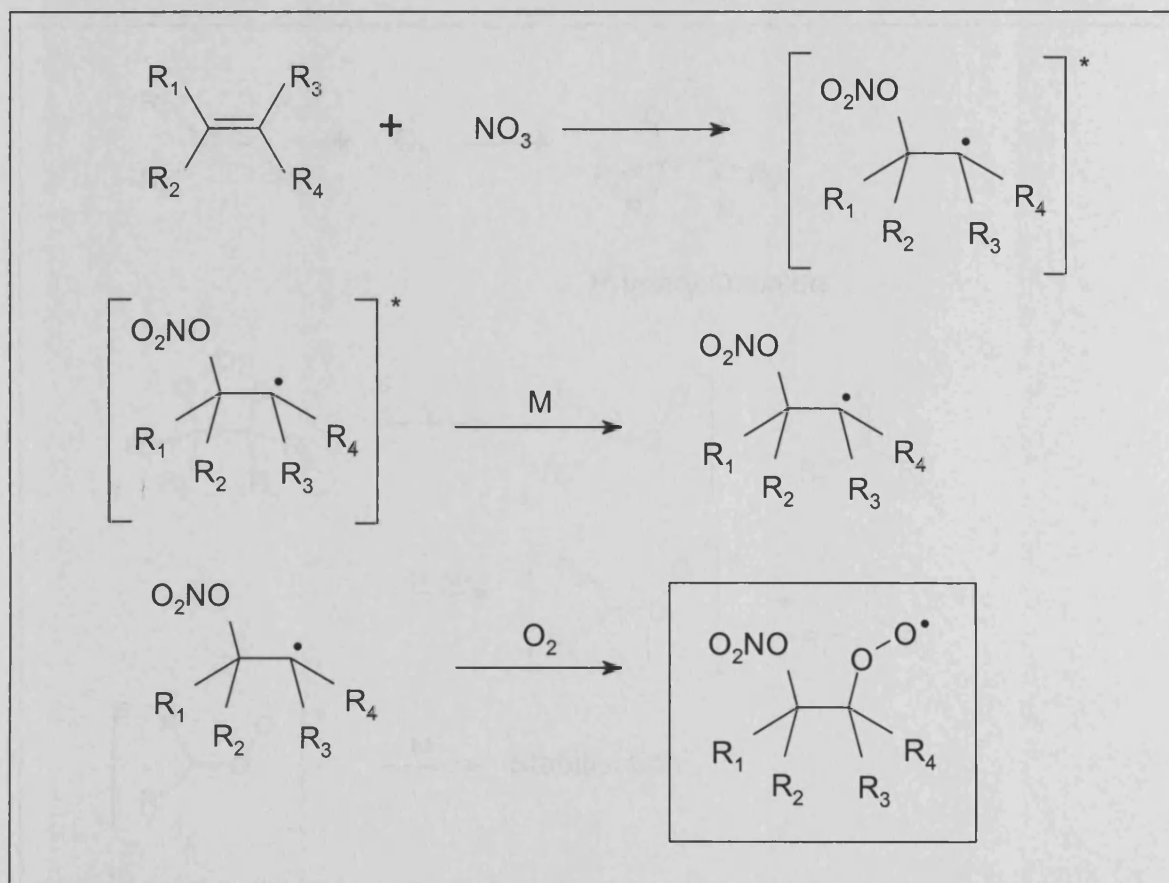
Although the hydroxyl radical (OH) is known to be the primary tropospheric oxidant in the daytime, there is mounting evidence in recent years that significant oxidation of volatile organic compounds (VOCs) can also occur at night in the lower atmosphere [e.g., Mihelcic *et al.*, 1993; Hu and Stedman, 1995; Paulson and Orlando, 1996; Cantrell *et al.*, 1997b; Carslaw *et al.*, 1997a,b]. One species believed to be central to this night-time chemistry is the nitrate radical (NO₃), formed by the relatively slow oxidation of NO₂ by O₃:



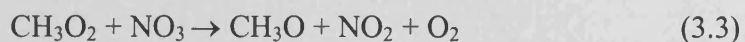
NO₃ absorbs strongly throughout the visible region of the spectrum, and is therefore rapidly photolysed during the day; it is estimated to have a lifetime of just 5 s for overhead sun and clear-sky conditions at sea-level [Orlando *et al.*, 1993]. At night, however, NO₃ can build up to significant mixing ratios *via* reaction (3.1). NO₃ reacts rapidly with unsaturated hydrocarbons, including butenes, pentenes and isoprene, as well as with reduced sulphur compounds, such as dimethyl sulphide (DMS) [Wayne *et al.*, 1991; Atkinson, 1994] to form peroxy radicals, HO₂ + RO₂ (see Figure 3.1, after Wayne *et al.*, [1991]), where R is an alkyl or acyl group [e.g., Platt *et al.*, 1990; Wayne *et al.*, 1991; Jensen *et al.*, 1992]. Indeed, Penkett *et al.* [1993] proposed that NO₃ could have a significant impact on the atmospheric lifetimes of many unsaturated hydrocarbons throughout the Northern Hemispheric troposphere.

Peroxy radicals can also be formed at night *via* reactions of ozone with alkenes [Hu and Stedman, 1995; Paulson and Orlando, 1996; Paulson *et al.*, 1999a,b; Rickard *et al.*, 1999]. Ozone adds to the double bond of the alkene in a concerted process, initially forming a primary ozonide (1,2,3-trioxolane), which rapidly decomposes to yield one or two carbonyl compounds and energy-rich Criegee intermediates. The vibrationally excited Criegee intermediate can then either be collisionally stabilised by a third body (M), or undergo unimolecular decomposition to products. It is now widely believed that alkyl-substituted Criegee intermediates can decompose *via* a vibrationally hot hydroperoxide intermediate to yield an OH radical, along with another radical species of the general form R₁R₂C'(O)R₃, which is expected to react rapidly with O₂ to form a peroxy radical (RO₂) [e.g., Martinez

Figure 3.1 Schematic representation of the mechanism for the reactions of the nitrate radical with alkenes [after Wayne *et al.*, 1991]



et al., 1981; Niki *et al.*, 1987; Rathman *et al.*, 1999]. The general mechanism is shown in schematic form in Figure 3.2 (a) [after Rickard *et al.*, 1999], whilst the specific example of propene oxidation is shown in Figure 3.2 (b). Once formed, peroxy radicals undergo further chemistry, as exemplified by the methylperoxy (CH_3O_2) radical:



The methoxy (CH_3O) radical so formed then reacts with O_2 to give HO_2 :



Figure 3.2 (a) Schematic representation of the mechanism for the reaction of ozone with a generalised alkene

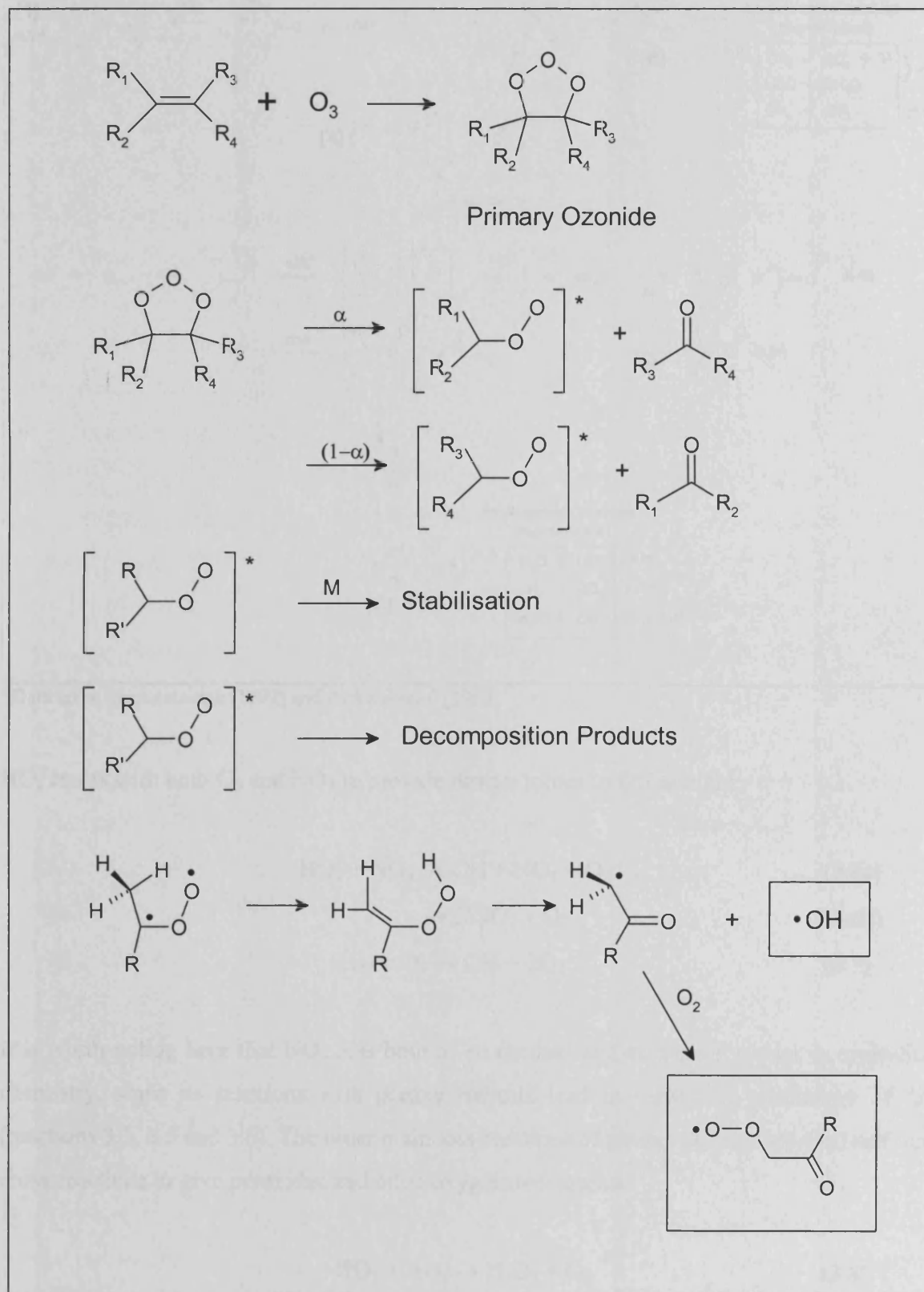
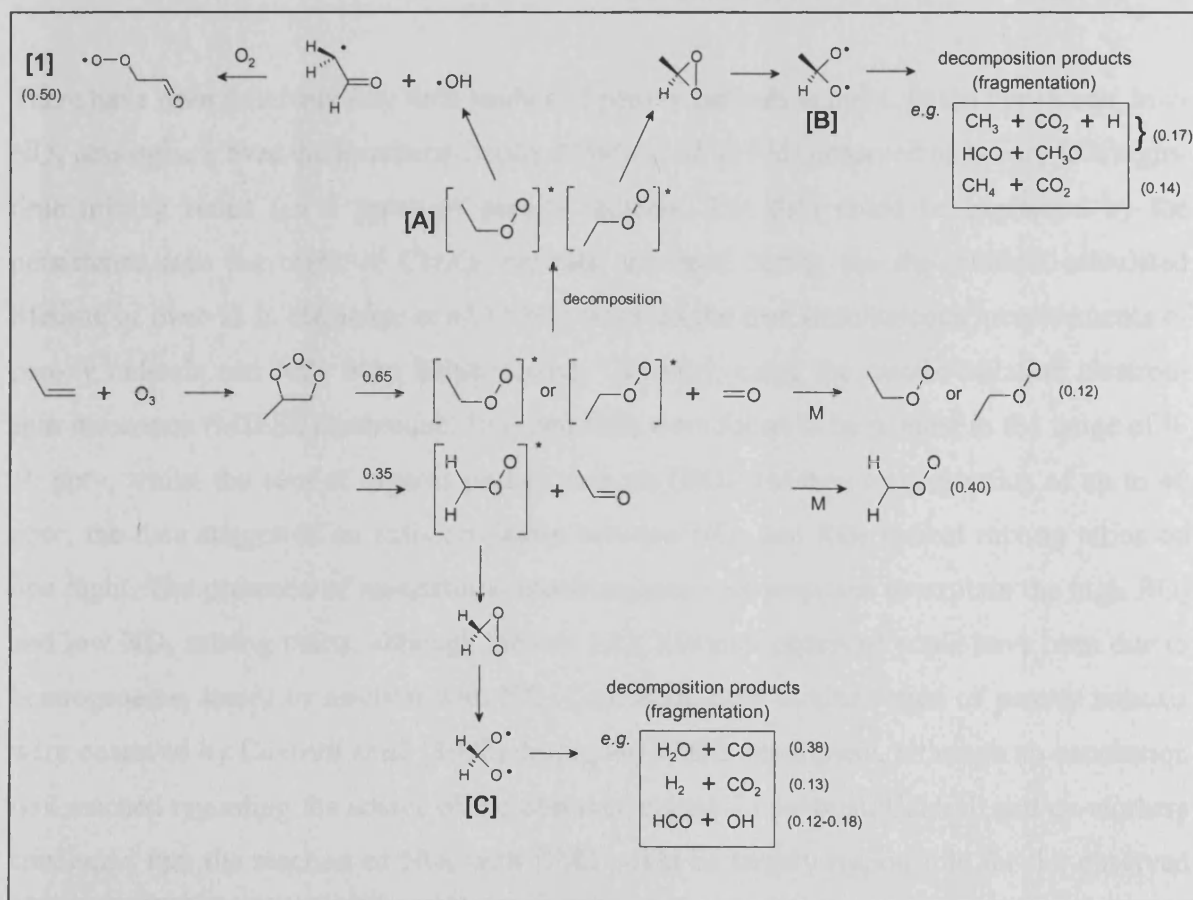
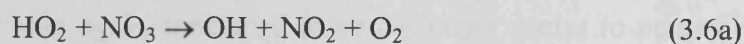


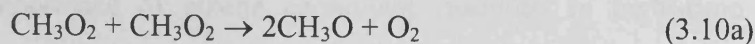
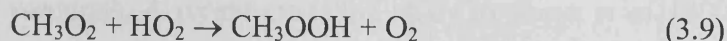
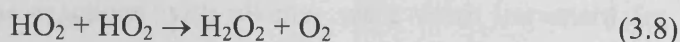
Figure 3.2 (b) Schematic representation of the reaction of ozone with propene^a

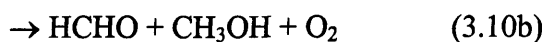
^a Data taken from Atkinson [1997] and Rickard *et al.* [1999].

HO_2 reacts with both O_3 and NO_3 to provide further routes to OH at night:



It is worth noting here that NO_3 acts both as an oxidant and as a chain carrier in night-time chemistry, since its reactions with peroxy radicals lead to night-time production of OH (reactions 3.3, 3.5 and 3.6). The other main loss reactions of peroxy radicals are their self- and cross-reactions to give peroxides and other oxygenated species:





There have been relatively few field studies of peroxy radicals at night. In the very clean, low- NO_x atmosphere over the Southern Ocean, *Monks et al.* [1996] observed only very low night-time mixing ratios (*ca* 1 pptv) of peroxy radicals. The data could be explained by the persistence into the night of CH_3O_2 radicals produced during the day, with a calculated lifetime of over 12 h. *Mihelcic et al.* [1993] reported the first simultaneous measurements of peroxy radicals and NO_3 from Schauinsland, Germany, using the matrix-isolation electron-spin resonance (MIESR) technique. NO_3 and HO_2 were found to be present in the range of 0-10 pptv, whilst the sum of organic peroxy radicals (RO_2) reached mixing ratios of up to 40 pptv; the data suggested an anti-correlation between NO_3 and RO_2 radical mixing ratios on one night. The presence of unmeasured monoterpenes was proposed to explain the high RO_2 and low NO_3 mixing ratios, although the low NO_3 lifetimes observed could have been due to heterogeneous losses or reaction with NO . Low night-time mixing ratios of peroxy radicals were observed by *Cantrell et al.* [1992] during the ROSE experiment, although no conclusion was reached regarding the source of the observed signal. In contrast, Cantrell and co-workers concluded that the reaction of NO_3 with DMS could be largely responsible for the observed peroxy radical signals at two sites where marine boundary layer air was frequently sampled, in Brittany [*Cantrell et al.*, 1996c] and Mauna Loa [*Cantrell et al.*, 1997b]. *Carslaw et al.* [1997b] observed a positive correlation between NO_3 and peroxy radicals measured at night at the coastal observatory in Weybourne, on the east coast of England. NO_3 reactions, particularly that with DMS, were again concluded to be the major routes to peroxy radical formation in the night-time.

Conversely, *Hu and Stedman* [1995] suggested that reactions of ozone with alkenes were largely responsible for peroxy radicals observed at night in Denver, Colorado in the summer of 1993, although no NO_x or VOC measurements were undertaken in this study. *Paulson and Orlando* [1996] used data from the ROSE experiment to model the potential importance of the reactions of O_3 with alkenes as radical sources both during the day and at night at a rural site. More recently, *Kanaya et al.* [1999] observed *ca* 3 pptv of HO_2 at night at Oki Island, Japan, and suggested that ozone reactions with alkenes were more important for peroxy radical production than NO_3 reactions. A recent modeling study by *Ariya et al.* [2000] also emphasised the possible importance of alkene ozonolysis reactions in night-time HO_x production.

This chapter presents a study of a substantial set of simultaneous observations of peroxy radicals and NO_3 made at the Mace Head Atmospheric Research Station, on the Atlantic coast of Ireland, during the Atmospheric Chemistry Studies in the Oceanic Environment (ACSOE) Eastern Atlantic Spring Experiment in April-May 1997 (EASE 97). These data, together with a comprehensive suite of volatile organic compound (VOC), ozone and ancillary measurements, are used to assess the relative importance of NO_3 and O_3 in the night-time oxidation of VOCs and production of peroxy radicals in the marine boundary layer. No account is taken in this chapter of the possible underestimation of peroxy radical mixing ratios by the PERCA instrument during EASE 97 (*cf.* Chapters 4 and 6), since the absolute mixing ratios are not crucial to the arguments presented here.

3.2 The EASE 97 Campaign

3.2.1 Measurement site

The EASE 97 campaign took place between 28th April and 29th May 1997 at the Mace Head Atmospheric Research Station, situated at 53.3 °N, 9.9 °W on the Atlantic coast of Ireland, 88 km west of Galway (see Figure 3.3). The station consists of two sets of buildings: one at 100 m from the shoreline with a 23 m tower for the air inlet of the ozone and carbon monoxide (CO) measurements; and another at 300 m from the shoreline at an altitude of 30 m above sea level [Carslaw *et al.*, 1999a]. During the campaign, there was also a 10 m tower at the upper site, where the inlet units for the NO_x , NO_y and PERCA measurements were situated, as well as a meteorological station at a height of 15 m above the ground. A 10 m tower near the shore buildings provided an inlet for hydrocarbon sampling, adjacent to the Fluorescence Assay by Gas Expansion (FAGE) instrument, which sampled hydroxyl (OH) and hydroperoxy (HO_2) radicals at 4.5 m above the ground. The Differential Optical Absorption Spectroscopy (DOAS) instrument for NO_3 measurements was situated at the near-shore site, with the retro-reflector array placed on a small island 4.2 km to the west of the station [Allan *et al.*, 2000b].

3.2.2 Other measurements

In addition to the PERCA peroxy radical measurements, OH and HO_2 were measured sequentially on two nights during EASE 97 using the Fluorescence Assay by Gas Expansion (FAGE) technique (see Chapter 1), with the instrument described by Creasey *et al.* [1997]. Further details of the deployment of this instrument in EASE 97 may be found in Carslaw *et al.* [2001a]. During EASE 97, the detection limits for the FAGE instrument were 0.02 pptv

for OH and 0.1 pptv for HO₂ (150 s averages, signal-to-noise ratio = 1). The overall 1 σ uncertainty for a 150 s average measurement was estimated to be 20% for OH and 25% for HO₂ [Carslaw *et al.*, 2001a].

NO₃ was measured using the Differential Optical Absorption Spectroscopy (DOAS) technique, as described by Allan *et al.* [1999, 2000a,b], with a mean 1 σ uncertainty of $\pm 15\%$ (1 h average). VOCs, including DMS, were measured by *in-situ* gas chromatographic techniques, as described by Lewis *et al.* [1996; 1997; 1999] and Grenfell *et al.* [1999a], with 1 σ uncertainties of ± 5 -10% (1 h average), depending on mixing ratio. Formaldehyde (HCHO) was measured by fluorimetric detection based on the Hantzsch reaction [Cárdenas *et al.*, 2000]. Ozone measurements were made using a commercial UV ($\lambda = 254$ nm) spectrometer, as described by Derwent *et al.* [1994], with an estimated accuracy of $\pm 5\%$. NO_x was measured using commercial CRANOX (Ecophysics) instrumentation, as described by Cárdenas *et al.* [1998]; in addition, more sensitive NO measurements were made using an instrument designed and built at the NOAA Aeronomy Laboratory, operated by the University of East Anglia (UEA), and described by Carpenter *et al.* [2000]; the measurements of the latter instrument were used in the work presented in this chapter (*cf.* Chapter 4). The UEA instrument was also used to measure NO₂ and NO_y. The accuracy of the UEA NO_x measurements has been estimated by Carpenter *et al.* [2000] to be $\pm 13\%$ for NO and $\pm 33\%$ for NO₂ (for ambient levels of 50 pptv and 150 pptv, respectively).

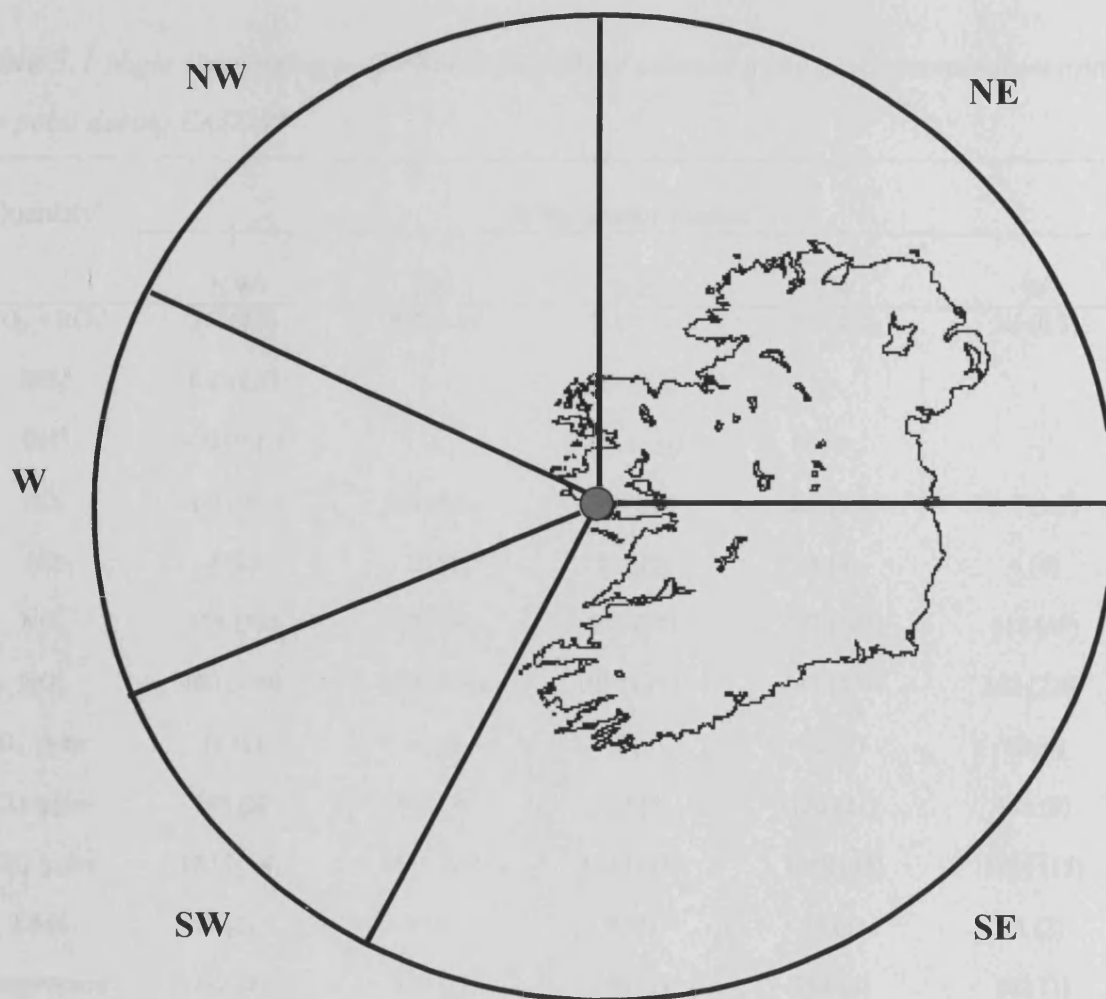
A fuller list of measurements undertaken during EASE 97 is shown in Table 4.1 of Chapter 4; a comprehensive site description of Mace Head, including photographs, can be found in Cvitaš and Kley [1994].

3.2.3 Data analysis

In order to examine the night-time chemistry occurring in differing air masses observed at Mace Head during the campaign, the data from EASE 97 were divided up according to incident wind direction at the site. Previous work at Mace Head has shown that the station regularly receives relatively clean air masses from southerly latitudes, the mid-Atlantic and the Arctic, as well as more polluted air masses advected from Britain and continental Europe [Simmonds *et al.*, 1997]. Five wind sectors were chosen for analysis: north-easterly (NE), 0-90°; south-easterly (SE), 90-200°; south-westerly (SW), 200-250°; westerly (W), 250-300°; and north-westerly (NW), 300-360°, as indicated in Fig. 3.3. The effects of local sea/coast breezes were removed from the analysis by selecting data only where the local wind speed

was over 3 m s^{-1} [cf. Cape *et al.*, 2000]. The data were allocated to wind sectors using the hourly averaging method described in Chapter 4, Section 4.2.1.

Figure 3.3 Map of Ireland showing the location of the Mace Head Atmospheric Research Station, and the wind sectors used in the data analysis (see Chapter 4, Section 4.2.1)



The hourly averaged data points were then used to derive averaged night-time profiles over the whole campaign for each wind sector. In this work, the night-time period was defined using the criterion of non-zero $[\text{NO}_3]$, and hence usually extended from 19:00 – 06:00. This criterion was chosen in preference to a strict definition based on solar zenith angles reaching 85 or 90° because the possible sources of peroxy radicals in the early morning and late evening are also generally little investigated. Table 3.1 shows the average night-time mixing ratios of selected species during EASE 97 by wind sector derived using this method. Table 3.2 shows the average night-time alkene mixing ratios by wind sector measured during EASE 97. The alkene measurements have been discussed in detail by Lewis *et al.* [1999];

nevertheless, it is worth noting here that the alkene mixing ratios were generally lower in the 'clean' wind sectors (NW, SW and W) than for the relatively polluted NE and SE sectors (Table 3.2), as would be expected from the oceanic origins of the air masses (see also Chapter 4). Ethene, propene and 2-methylpropene levels, however, remained significant, even in 'clean' marine air. *Lewis et al.* [1999] proposed that these species had emission sources from coastal waters local to Mace Head, *via* photodegradation of organic carbon in sea water.

Table 3.1 Night-time averages (1900-0600 GMT) of selected trace gases, temperature and dew point during EASE 97

Quantity ^a	Wind sector means ^b				
	NW	NE	SE	SW	W
HO ₂ + RO ₂ ^c	3.7 (0.9)	5.7 (0.9)	5.4 (1.4)	3.8 (1.4)	2.6 (0.5)
HO ₂ ^d	0.6 (0.1)	-	1.4 (0.3)	-	-
OH ^d	< 0.01 (-)	-	< 0.01 (-)	-	-
NO ₃	2.0 (0.9)	3.0 (1.8)	5.0 (2.9)	2.6 (2.1)	3.7 (1.8)
NO	4 (4)	6 (5)	14 (17)	4 (4)	4 (4)
NO ₂	135 (38)	253 (133)	814 (91)	192 (141)	118 (45)
NO _y	460 (170)	820 (318)	1952 (335)	547 (477)	492 (229)
O ₃ /ppbv	38 (2)	34 (2)	37 (3)	33 (7)	32 (4)
CO /ppbv	142 (3)	155 (7)	157 (5)	136 (21)	147 (8)
CH ₄ /ppbv	1825 (14)	1841 (13)	1847 (16)	1819 (35)	1824 (15)
DMS	9 (2)	9 (2)	9 (2)	18 (5)	11 (2)
Temperature /K	282 (1)	283 (1)	285 (1)	284 (1)	282 (1)
Dew point /K	281 (1)	280 (1)	282 (1)	283 (2)	282 (1)

^a All values are in pptv except where indicated.

^b Figures in parentheses are 1 σ values.

^c Measurements made using the PERCA technique.

^d Measurements made using the FAGE technique: two nights only (see Section 3.4.3).

3.3 The Nitrate Radical during EASE 97

The mixing ratios of NO₃ observed during EASE 97 ranged from 1-5 pptv in relatively clean, marine air masses to 1-40 pptv in semi-polluted conditions [*Allan et al.*, 2000b]. These differences are reflected to some extent in the average mixing ratios shown in Table 3.1 (*e.g.*, 5.0 in the SE wind sector; 2.6 pptv in the SW wind sector), and arose from changes in both

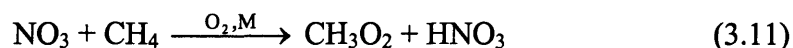
the production rate (reaction 3.1) and total loss rate of the species. Loss pathways for NO_3 at night include not only reaction with unsaturated VOCs, DMS and peroxy radicals, as described previously, but also reaction with methane (reaction 3.11) and further reaction with NO_2 to give N_2O_5 (reaction 3.12), which may be lost by hydrolysis in the gas phase (reaction 3.13) and by uptake on aerosols [*e.g.*, Carslaw *et al.*, 1997b; Allan *et al.*, 2000b].

Table 3.2 Night-time averages (1900-0600 GMT) of alkenes measured during EASE 97

Alkene ^a	Wind Sector Means ^b				
	NW	NE	SE	SW	W
Ethene	25 (4)	37 (9)	44 (7)	26 (13)	36 (14)
Propene	17 (3)	27 (11)	37 (4)	20 (10)	21 (5)
<i>trans</i> -but-2-ene	2 (2)	2 (1)	2 (1)	2 (3)	0 (1)
But-1-ene	2 (2)	6 (3)	9 (1)	4 (6)	2 (2)
2-Methylpropene	7 (1)	13 (5)	13 (2)	8 (3)	7 (2)
<i>cis</i> -but-2-ene	3 (3)	5 (1)	4 (1)	2 (4)	1 (2)
1,3-butadiene	1 (1)	4 (2)	7 (2)	1 (3)	2 (2)
<i>trans</i> -pent-2-ene	1 (1)	2 (1)	1 (1)	0 (1)	0 (0)
<i>cis</i> -pent-2-ene	0 (1)	1 (1)	1 (1)	1 (1)	0 (0)
Isoprene	0 (1)	1 (1)	1 (1)	0 (0)	0 (1)

^a All values are in pptv.

^b Figures in parentheses are 1σ values.



The equilibrium between NO_3 and N_2O_5 is established rapidly at ambient temperatures, unless NO_2 mixing ratios are very low [Carslaw *et al.*, 1997a; Allan *et al.*, 2000b], so that any losses of N_2O_5 effectively represent losses of NO_3 .

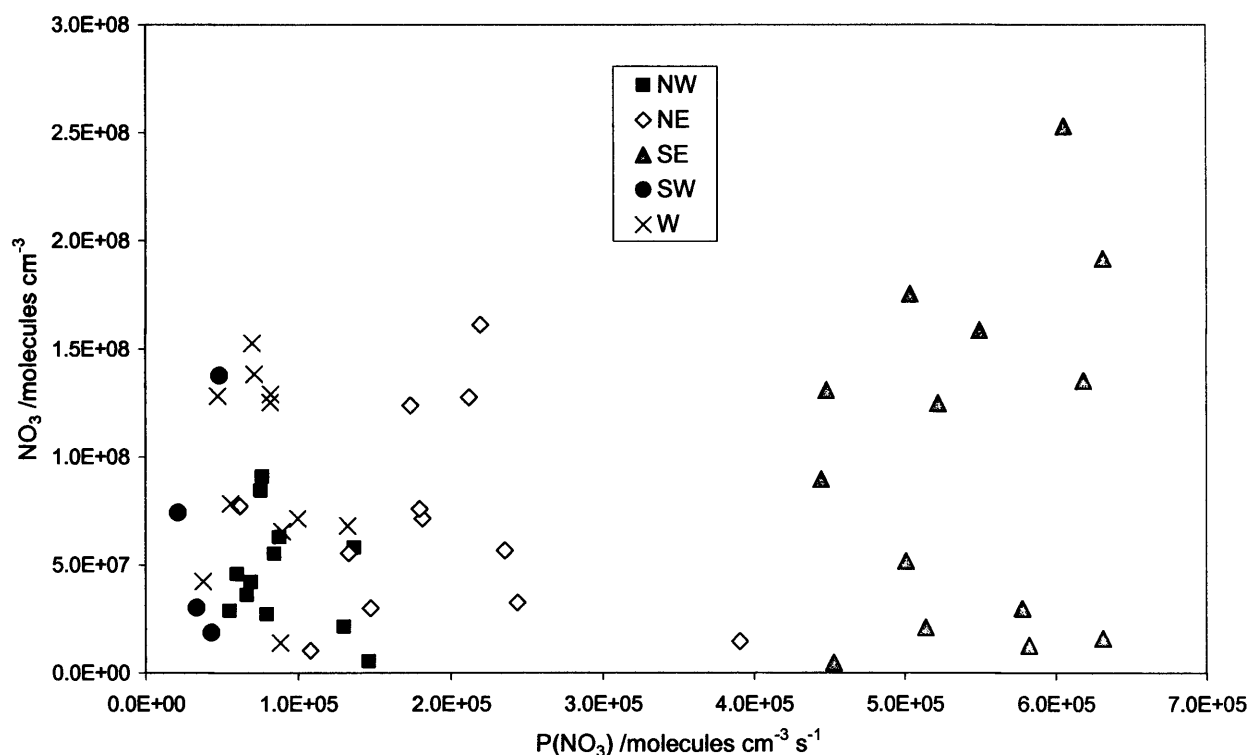
Table 3.1 shows that the average NO_2 mixing ratio, and hence the average rate of NO_3 production ($\text{P}(\text{NO}_3) = k_1[\text{NO}_2][\text{O}_3]$) was much higher at night in the SE wind sector than in any of the other sectors. This point is illustrated in Figure 3.4, which shows a scatter plot of $\text{P}(\text{NO}_3)$ versus $[\text{NO}_3]$ by wind sector, where each point represents a composite wind sector hourly average. Although there is significant scatter in Fig. 3.4, positive correlation between $\text{P}(\text{NO}_3)$ and $[\text{NO}_3]$ is discernible, particularly in the maximum $[\text{NO}_3]$ observed in each wind

sector. Such a correlation is expected if there are significant direct removal processes of the nitrate radical [Heintz *et al.*, 1996; Allan *et al.*, 1999], since in such a case, assuming steady state is achieved:

$$P(\text{NO}_3) = k_1[\text{NO}_2][\text{O}_3] = L(\text{NO}_3) = \{\sum k_i[\text{X}_i]\}[\text{NO}_3] \quad (3.14)$$

where X_i is a species which reacts with NO_3 with rate coefficient k_i . If no correlation between $P(\text{NO}_3)$ and $[\text{NO}_3]$ is observed, indirect loss of NO_3 via N_2O_5 is likely to be dominant [Allan *et al.*, 1999].

Figure 3.4 Scatter plot of $P(\text{NO}_3)$ ($=k_1[\text{NO}_2][\text{O}_3]$) versus $[\text{NO}_3]$ by wind sector



A useful, closely related way of examining the behaviour of NO_3 is to calculate its turnover lifetime, $\tau(\text{NO}_3)$, which applies assuming that NO_3 is in steady state:

$$\tau(\text{NO}_3) = \frac{[\text{NO}_3]}{k_1[\text{NO}_2][\text{O}_3]} \quad (3.15)$$

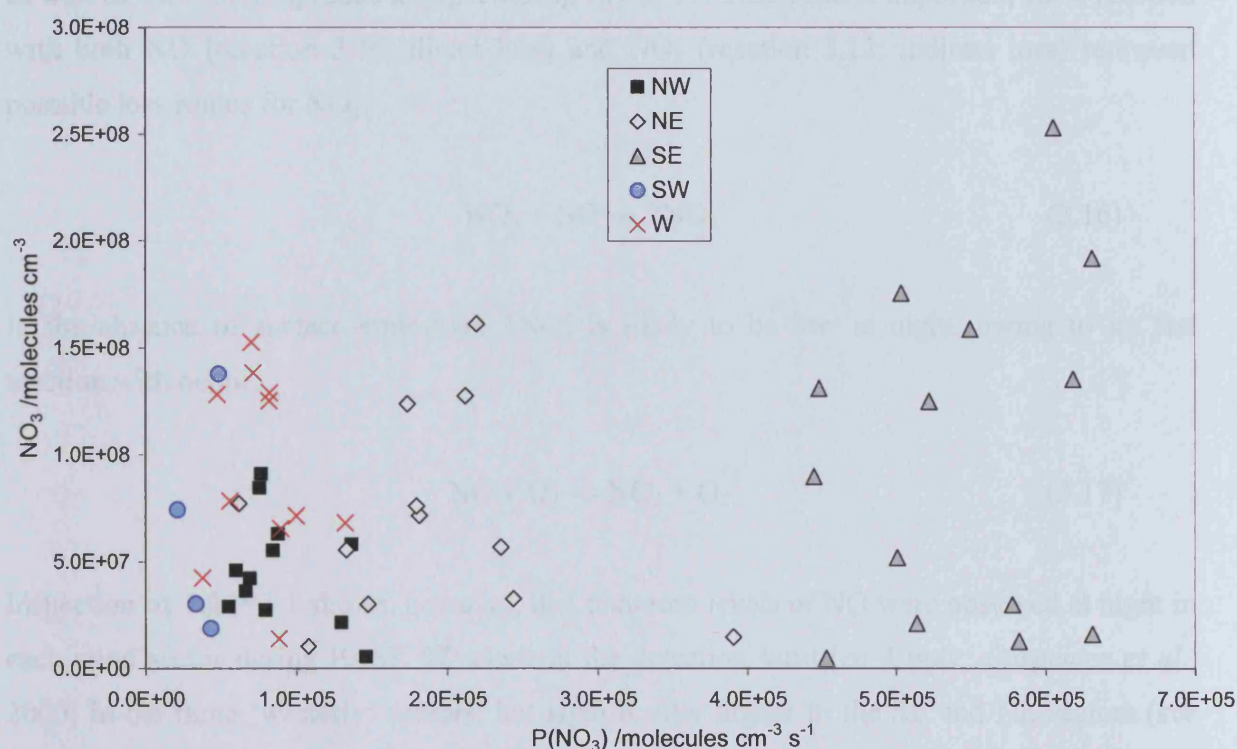
The mean lifetimes obtained using Equation (3.15) for each wind sector in EASE 97 are given in Table 3.3.

sector. Such a correlation is expected if there are significant direct removal processes of the nitrate radical [Heintz *et al.*, 1996; Allan *et al.*, 1999], since in such a case, assuming steady state is achieved:

$$P(\text{NO}_3) = k_1[\text{NO}_2][\text{O}_3] = L(\text{NO}_3) = \{\sum k_i[\text{X}_i]\}[\text{NO}_3] \quad (3.14)$$

where X_i is a species which reacts with NO_3 with rate coefficient k_i . If no correlation between $P(\text{NO}_3)$ and $[\text{NO}_3]$ is observed, indirect loss of NO_3 via N_2O_5 is likely to be dominant [Allan *et al.*, 1999].

Figure 3.4 Scatter plot of $P(\text{NO}_3)$ ($=k_1[\text{NO}_2][\text{O}_3]$) versus $[\text{NO}_3]$ by wind sector



A useful, closely related way of examining the behaviour of NO_3 is to calculate its turnover lifetime, $\tau(\text{NO}_3)$, which applies assuming that NO_3 is in steady state:

$$\tau(\text{NO}_3) = \frac{[\text{NO}_3]}{k_1[\text{NO}_2][\text{O}_3]} \quad (3.15)$$

The mean lifetimes obtained using Equation (3.15) for each wind sector in EASE 97 are given in Table 3.3.

Table 3.3 Mean NO₃ turnover lifetimes by wind sector during EASE 97

Wind sector	$\tau(\text{NO}_3)$ /min
NW	10.7
NE	7.3
SE	3.5
SW	31.9
W	22.1

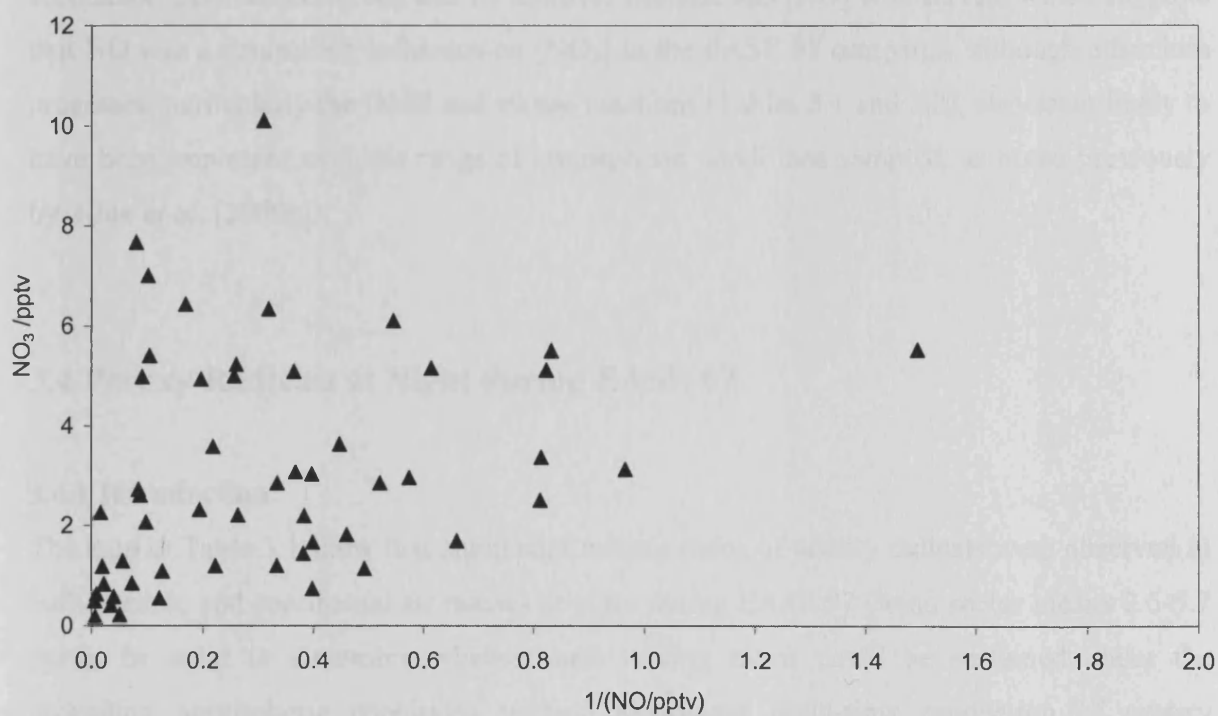
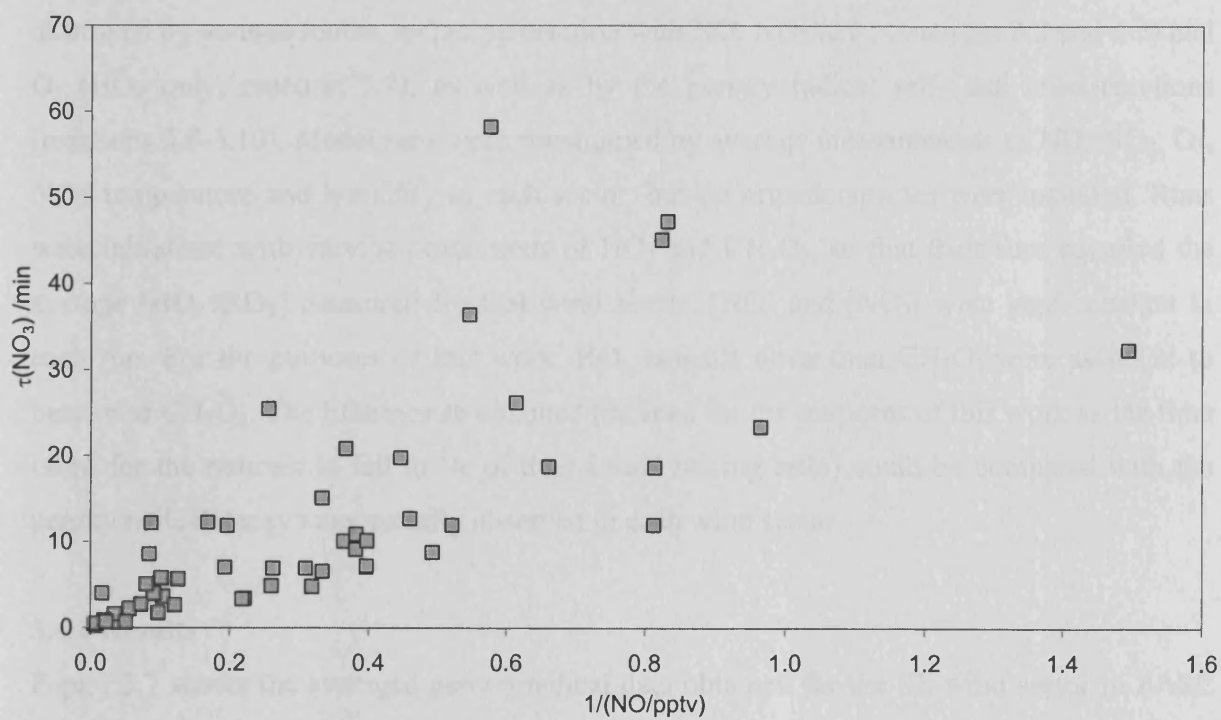
The data in Table 3.3 show that the longest lifetimes were observed in the three, relatively clean ‘westerly’ wind sectors, NW, SW and W (see also Fig. 3.4). Comparison with Table 3.1 indicates that these three sectors were generally the least polluted in terms of NO_x (NO+NO₂) as well as VOC mixing ratios at night during EASE 97. This point is important, since reaction with both NO (reaction 3.16; direct loss) and NO₂ (reaction 3.12; indirect loss) represent possible loss routes for NO₃.



In the absence of surface emissions, [NO] is likely to be low at night, owing to its fast reaction with ozone:



Inspection of Table 3.1 shows, however, that non-zero levels of NO were observed at night in each wind sector during EASE 97: close to the detection limit [*ca* 4 pptv; *Carpenter et al.*, 2000] in the three ‘westerly’ sectors, but significantly higher in the SE and NE sectors (see Section 3.4.2 for further discussion of this point). Nevertheless, it must be noted that the average figures in Table 3.1 include the dawn and dusk periods as well as night proper. The relationship between [NO₃] and the reciprocal of [NO] during EASE 97 is shown in Figure 3.5, whilst Figure 3.6 shows a similar plot where [NO₃] is replaced by the turnover lifetime, $\tau(\text{NO}_3)$. In both Figs 3.5 and 3.6, each point is a composite wind sector hour, as for Fig. 3.4.

Figure 3.5 Scatter plot of NO_3 and reciprocal NO mixing ratios during EASE 97**Figure 3.6** Scatter plot of NO_3 lifetime, $\tau(\text{NO}_3)$, and reciprocal NO mixing ratios during EASE 97

Once again there is a high degree of scatter in both Figs 3.5 and 3.6; nevertheless, a clear anti-correlation between both NO_3 and its turnover lifetime and $[\text{NO}]$ is observed, which suggests that NO was a controlling influence on $[\text{NO}_3]$ in the EASE 97 campaign, although other loss processes, particularly the DMS and alkene reactions (Tables 3.1 and 3.2), also seem likely to have been important over the range of atmospheric conditions sampled, as noted previously by *Allan et al.* [2000b].

3.4 Peroxy Radicals at Night during EASE 97

3.4.1 Introduction

The data in Table 3.1 show that significant mixing ratios of peroxy radicals were observed in both oceanic and continental air masses at night during EASE 97 (wind sector means 2.6–5.7 pptv). In order to determine whether such mixing ratios could be sustained under the prevailing atmospheric conditions without significant night-time production of peroxy radicals, a simple peroxy radical lifetime modelling study was carried out for each wind sector using the FACSIMILE for Windows package [*AEA Technology*, 1995], as described in Chapter 2, and the reaction scheme shown in Table 3.4. This method was employed in preference to estimations of lifetimes by direct calculation, as peroxy radicals can be destroyed by various routes, including reaction with NO , NO_3 (e.g., reactions 3.2 and 3.3) and O_3 (HO_2 only; reaction 3.7), as well as by the peroxy radical self- and cross-reactions (reactions 3.8–3.10). Model runs were constrained by average measurements of NO , NO_2 , O_3 , NO_3 , temperature and humidity in each sector, but no organic species were included. Runs were initialised with various proportions of HO_2 and CH_3O_2 , so that their sum equalled the average $[\text{HO}_2 + \text{RO}_2]$ measured for that wind sector. $[\text{NO}]$ and $[\text{NO}_3]$ were kept constant in each run. For the purposes of this work, RO_2 radicals other than CH_3O_2 were assumed to behave as CH_3O_2 . The lifetimes so obtained (defined for the purposes of this work as the time taken for the radicals to fall to $1/e$ of their initial mixing ratio) could be compared with the peroxy radical decay rates actually observed in each wind sector.

3.4.2 Results

Figure 3.7 shows the averaged peroxy radical data obtained for the SE wind sector in EASE 97; $j(\text{NO}_2)$, the photolysis rate coefficient of NO_2 , is plotted on a secondary axis in Fig. 3.7 for comparison. The daytime maximum was not at solar noon, as found under relatively unpolluted conditions [e.g., *Monks et al.*, 2000], but rather mid-afternoon (Fig. 3.7 (a)). This

effect was probably due to relatively elevated NO levels in the morning (not shown in Fig. 3.7), which acted to suppress peroxy radical mixing ratios (reactions 3.2, 3.5 and 3.18; see also Chapter 4, Section 4.4), as well as enhanced peroxy radical production from sources other than ozone photolysis in the afternoon, *e.g.*, formaldehyde photolysis (see Chapter 5, Section 5.6).

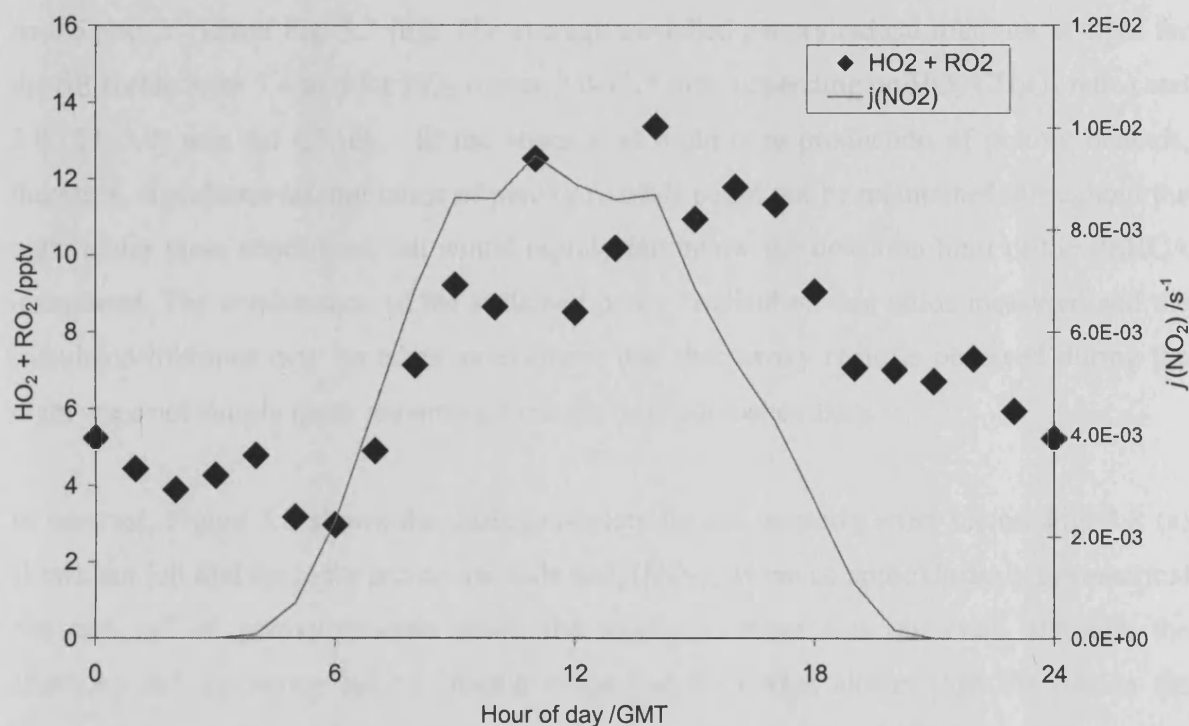
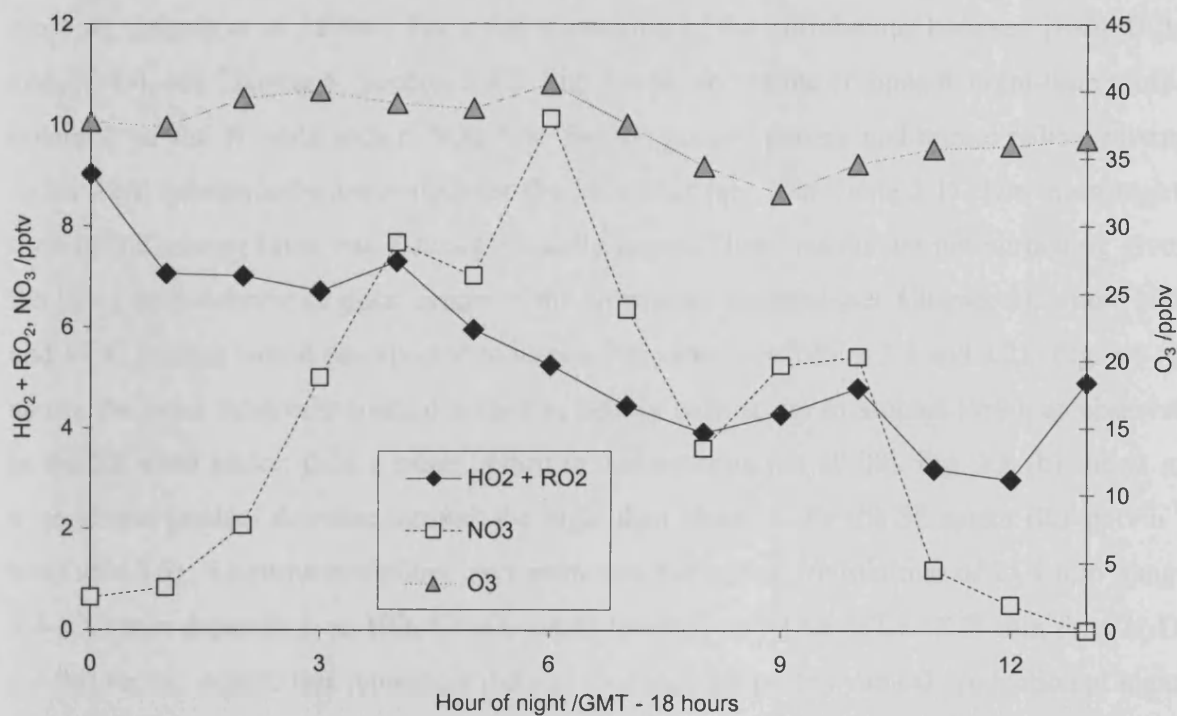


Table 3.4 Reaction scheme used in the modelling of the night-time peroxy radical lifetimes

Reaction	Rate expression /cm ³ molecule ⁻¹ s ⁻¹ except [†] s ⁻¹
HO ₂ + NO → OH + NO ₂	3.7E-12*EXP(250/T)
OH + NO + M → HONO + M	Troe expression ^a
OH + NO ₂ + M → HONO ₂ + M	Troe expression ^a
OH + HONO → H ₂ O + NO ₂	1.8E-11*EXP(-390/T)
HO ₂ + NO ₂ + M → HO ₂ NO ₂ + M	Troe expression ^a
OH + H ₂ O ₂ → HO ₂ + H ₂ O	2.9E-12*EXP(-160/T)
HO ₂ + OH → H ₂ O + O ₂	4.8E-11*EXP(250/T)
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	(2.3E-13*EXP(600/T) + 1.7E-33 * [M]*EXP(1000/T))* (1 + 1.4E-21 * [H ₂ O]*EXP(2200/T))
OH + O ₃ → HO ₂ + O ₂	1.6E-12*EXP(-940/T)
HO ₂ + O ₃ → OH + O ₂ + O ₂	1.1E-14*EXP(-500/T))
NO + O ₃ → NO ₂ + O ₂	2.0E-12*EXP(-1400/T)
HO ₂ + CH ₃ O ₂ → CH ₃ O ₂ H + O ₂	3.8E-13*EXP(800/T)
CH ₃ O ₂ + NO → CH ₃ O + NO ₂	4.2E-12*EXP(180/T)
CH ₃ O + NO + M → CH ₃ ONO + M	Troe expression ^a
CH ₃ O + NO ₂ → HCHO + HONO	1.1E-11*EXP(-1200/T)
CH ₃ O + NO ₂ + M → CH ₃ ONO ₂ + M	Troe expression ^a
CH ₃ O + O ₂ → HCHO + HO ₂	3.9E-14*EXP(-900/T)
HO ₂ + NO ₃ → OH + NO ₂ + O ₂	3.0E-12 ^b
CH ₃ O ₂ + NO ₃ → CH ₃ O + NO ₂ + O ₂	1.0E-12 ^c
NO ₂ + O ₃ → NO ₃ + O ₂	1.2E-13*EXP(-2450/T)
OH + HO ₂ NO ₂ → H ₂ O + NO ₂ + O ₂	1.3E-12*EXP(380/T)
OH + HONO ₂ → H ₂ O + NO ₃	7.2E-15*EXP(785/T) + 4.1E-16 *EXP(1440/T)
OH + NO ₃ → HO ₂ + NO ₂	2.2E-11
OH + OH → H ₂ O + O	4.2E-12*EXP(-240/T)
OH + OH + M → H ₂ O ₂ + M	Troe expression ^a
CH ₃ O ₂ + CH ₃ O ₂ → CH ₃ O + CH ₃ O	1.0E-13*EXP(220/T)
CH ₃ O ₂ + CH ₃ O ₂ → CH ₃ OH + HCHO	6.8E-14*EXP(220/T)
NO + NO ₃ → NO ₂ + NO ₂	1.5E-11*EXP(170/T)
NO ₂ + NO ₃ + M → N ₂ O ₅ + M	Troe expression ^a
N ₂ O ₅ → NO ₂ + NO ₃	1.0E-3*EXP(-11000/T)*[M] [†]
HO ₂ NO ₂ → HO ₂ + NO ₂	8.62E-2 ^{d†}
CH ₃ ONO ₂ → CH ₃ O + NO ₂	3.50E-1 ^{d†}

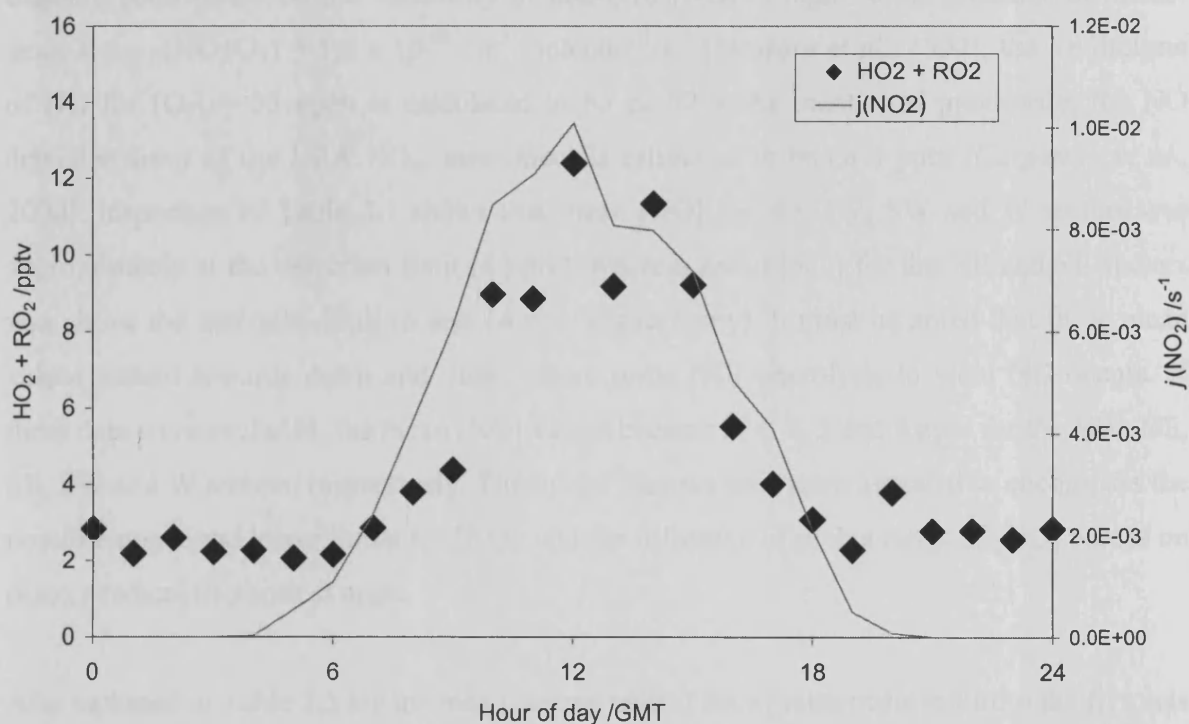
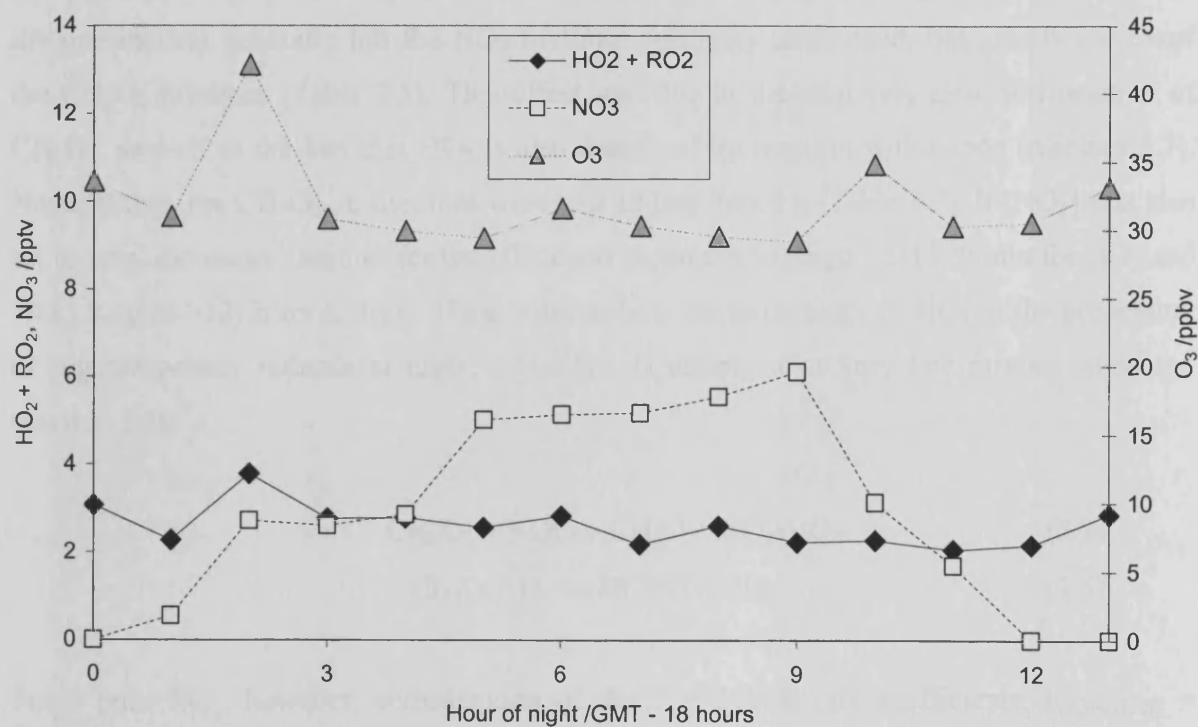
^aTermolecular rate coefficients were converted into bimolecular rate coefficients $k(\text{M}, \text{T})$ using the Troe expression recommended by DeMore *et al.* [1997].

^b Mellouki *et al.* [1993]. ^c Biggs *et al.* [1994]. ^d Atkinson [1997].

Figure 3.7 Composite profiles of data collected in the SE wind sector(a) Diel cycles of $[\text{HO}_2 + \text{RO}_2]$ and $j(\text{NO}_2)$ (b) Night-time profiles of $[\text{HO}_2 + \text{RO}_2]$, $[\text{NO}_3]$ and $[\text{O}_3]$ 

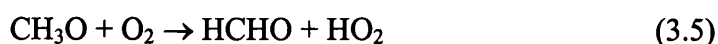
As a result of this ‘delayed’ maximum in photochemical activity, the peroxy radical mixing ratios were still relatively high in the late afternoon (Fig. 3.7 (b)). After dropping off rapidly between 16:00 and 19:00, the peroxy radical mixing ratios stabilised, even increased slightly, between 19:00 and 22:00, and then decreased only slowly through the night, at a mean rate of *ca* 0.5 pptv h⁻¹ (from Fig. 3.7 (b)). The average modelled peroxy radical lifetimes at night for the SE sector were 5.4 min for HO₂ (range 2.0-11.5 min, depending on HO₂/CH₃O₂ ratio) and 3.0 (2.9-3.0) min for CH₃O₂. In the absence of night-time production of peroxy radicals, therefore, significant mixing ratios of peroxy radicals could not be maintained throughout the night under these conditions, but would rapidly fall below the detection limit of the PERCA instrument. The combination of the sustained peroxy radical mixing ratios measured and the calculated lifetimes may be taken as evidence that the peroxy radicals observed during the night were not simply those remaining from daytime photochemistry.

In contrast, Figure 3.8 shows the analogous plots for the westerly wind sector. Fig. 3.8 (a) shows the full diel cycle for peroxy radicals and $j(\text{NO}_2)$, where an approximately symmetrical rise and fall of peroxy radicals about the solar maximum was observed, although the afternoon fall in peroxy radical mixing ratios was somewhat slower than the rise in the morning. This effect is due to the relatively slow self-reaction of CH₃O₂ (and any other organic peroxy radicals present), and has the consequence that afternoon peroxy radical mixing ratios correlate less well with the photolysis rate of ozone $j(\text{O}^1\text{D})$ than those in the morning [Monks *et al.*, 1996]. For a full discussion of the correlations between [HO₂+RO₂] and $j(\text{O}^1\text{D})$, see Chapter 5, Section 5.3.2. Fig. 3.8 (b) shows the composite night-time profile obtained for the W wind sector. Note first that the general peroxy and nitrate radical mixing ratios were substantially lower than for the SE sector (see also Table 3.1). The mean night-time ozone mixing ratio was also significantly lower. These results are not surprising given the likely mid-Atlantic or polar origin of the air masses sampled (see Chapter 4), where NO_x and VOC loading would be expected to be relatively low (see Tables 3.1 and 3.2). Fig. 3.8 (a) shows the same relatively sharp decrease in peroxy radicals up to around 19:00, as observed in the SE wind sector, then a small upturn in mid-evening (*ca* 20:00). Fig. 3.8 (b) shows an even slower gradual decrease through the night than observed for the SE sector (0.1 pptv h⁻¹; see Table 3.5). Lifetime modelling gave estimated theoretical ¹/_e lifetimes of 25.4 min (range 9.4-59.2 min depending on HO₂/CH₃O₂ ratio) for HO₂ and 17.6 (17.1-18.2) min for CH₃O₂ for this sector. Again, this represents indirect evidence for peroxy radical production at night, even under the relatively clean conditions of the W wind sector, albeit giving much lower mixing ratios than under more polluted conditions.

Figure 3.8 Composite profiles of data collected in the W wind sector(a) Diel cycles of $[\text{HO}_2 + \text{RO}_2]$ and $j(\text{NO}_2)$ (b) Night-time profiles of $[\text{HO}_2 + \text{RO}_2]$, $[\text{NO}_3]$ and $[\text{O}_3]$ 

Similar results were obtained for the other three wind sectors (not shown). Table 3.5 gives the modelled peroxy radical lifetimes obtained for each sector, using both the mean measured NO mixing ratios and with [NO] set to zero. This dual procedure was adopted because there is ongoing controversy on the feasibility of non-zero [NO] at night in the presence of ozone: since $k_{(T=285)}(\text{NO}+\text{O}_3) = 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [DeMore *et al.*, 1997], the $1/e$ lifetime of NO for $[\text{O}_3] = 35 \text{ ppbv}$ is calculated to be *ca* 77 s. As mentioned previously, the NO detection limit of the UEA NO_x instrument is estimated to be *ca* 4 pptv [Carpenter *et al.*, 2000]. Inspection of Table 3.1 shows that mean [NO] for the NW, SW and W sectors was approximately at the detection limit (4 pptv), whereas mean [NO] for the NE and SE sectors was above the detection limit (6 and 14 pptv respectively). It must be noted that these mean values extend towards dawn and dusk, where some NO_2 photolysis to yield NO occurs. If these data were excluded, the mean [NO] values became 2, 4, 8, 2 and 4 pptv for the NW, NE, SE, SW and W sectors, respectively. The model lifetime runs were intended to encompass the possible upper and lower limits for [NO], and the influence of such a range of [NO] values on peroxy radical lifetimes at night.

Also included in Table 3.5 are the mean peroxy radical decay rates observed from the five sets of experimental data. It is worth noting that the lowest modelled lifetimes were observed in the SE sector, where $[\text{NO}_x]$ was highest. The CH_3O_2 lifetimes for the three ‘westerly’ sectors (SW, W and NW) were all quite similar, at around 12-18 min. Setting [NO] to zero in the lifetime models generally left the HO_2 lifetimes relatively unchanged, but greatly increased the CH_3O_2 lifetimes (Table 3.5). This effect was due to the relatively slow self-reaction of CH_3O_2 , as well as the fact that HO_2 is also destroyed by reaction with ozone (reaction 3.7). Nevertheless, the CH_3O_2 $1/e$ lifetimes were still all less than 3 h (Table 3.5). If $[\text{NO}_3]$ was also set to zero, the mean lifetimes for the NE sector became 8.5 (range 7.2-11.9) min for HO_2 and >4 (3.8 up to >12) h for CH_3O_2 . These results show the importance of NO_3 to the processing of organic peroxy radicals at night, when NO is absent or at very low mixing ratios (*cf.* reaction 3.2):



For 5 pptv NO_3 , however, consideration of the $T = 298 \text{ K}$ rate coefficients, $k_{\text{NO}+\text{CH}_3\text{O}_2} = 7.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [DeMore *et al.*, 1997] and $k_{\text{NO}_3+\text{CH}_3\text{O}_2} = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$

s^{-1} [Mellouki *et al.*, 1993], shows that only 0.7 pptv NO is required for the $\text{CH}_3\text{O}_2 \rightarrow \text{HO}_2$ conversion rates to be equal *via* the two routes.

Table 3.5 Modelled peroxy radical lifetimes at night during EASE 97

Wind sector	Modelled τHO_2 /min ^a			Modelled $\tau\text{CH}_3\text{O}_2$ /min ^a			Observed $\text{HO}_2 + \text{RO}_2$ decay rate /pptv h ⁻¹
	Max.	Min.	Mean	Max.	Min.	Mean	
NW	46.4 (27.8)	6.6 (9.1)	21.1 (13.9)	12.6 (178.9)	11.9 (148.0)	12.3 (162.4)	0.4 (0.0) ^c
NE	33.8 (20.6)	4.7 (6.8)	13.1 (9.9)	10.2 (124.7)	9.4 (101.2)	9.8 (112.1)	0.1
SE	11.5 (14.7)	2.0 (5.9)	5.4 (8.0)	3.0 (98.8)	2.9 (86.6)	3.0 (92.7)	0.5 (0.0) ^b
SW	37.4 (17.3)	6.8 (9.2)	14.7 (11.3)	14.9 (153.9)	13.8 (130.0)	14.3 (142.9)	0.2
W	59.2 (59.6)	9.4 (12.2)	25.4 (22.6)	18.2 (120.7)	17.1 (117.1)	17.6 (118.9)	0.1

^a Figures in brackets assume $[\text{NO}] = 0$.

^b Observed HO_2 decay rate for the night 1st-2nd May (see Section 3.4.3).

^c Observed HO_2 decay rate for the night 21st-22nd May (see Section 3.4.3).

In summary, slow net decay of peroxy radical mixing ratios was observed during the night for the whole data set classified by wind sector: the observed decay rates (Table 3.5) imply $1/e$ lifetimes of 5.9, 34.7, 6.6, 11.4 and 16.1 h (mean 14.9 h) for peroxy radicals in the five wind sectors NW, NE, SE, SW and W, respectively. Conversely, the modelled peroxy radical $1/e$ lifetimes using average measured $[\text{NO}]$, which take into account all the known loss reactions for peroxy radicals, were less than 1 h for all wind sectors. Even with $[\text{NO}]$ set to zero, the average HO_2 lifetimes were only 8.0-22.6 min, whilst the average CH_3O_2 lifetimes were all < 3 h. In the absence of peroxy radical production at night, therefore, the peroxy radical mixing ratios would fall below the detection limit of the PERCA instrument in the course of the night. This analysis shows that the peroxy radicals observed at night during EASE 97 were not simply those remaining from daytime photochemistry. It may be inferred, therefore, that peroxy radicals were produced in significant mixing ratios at night during EASE 97.

3.4.3 Comparison with University of Leeds FAGE HO_2 and OH measurements

University of Leeds Fluorescence Assay by Gas Expansions (FAGE) HO_2 and OH data were also available for two nights during EASE 97. On the night of the 1st-2nd May, the HO_2

mixing ratios varied between *ca* 1-2 pptv (hourly averages), giving an average $[\text{HO}_2]/[\text{HO}_2+\text{RO}_2]$ ratio of 0.36. The other night on which HO_2 was measured was the 21st-22nd May, where $[\text{HO}_2]$ varied between 0.5 and 0.7 pptv, and the $[\text{HO}_2]/[\text{HO}_2+\text{RO}_2]$ ratio was lower throughout, with an average value of 0.18. The HO_2 measurements are plotted with the PERCA $[\text{HO}_2+\text{RO}_2]$ measurements in Figures 3.9 (a) 1st-2nd May; and (b) 21st-22nd May. The mean $[\text{HO}_2]/[\text{HO}_2+\text{RO}_2]$ ratio over both nights was 0.27; it must be remembered, however, that the likely effect of humidity on the PERCA measurements during EASE 97 (see Chapters 2 and 6) means that the ratios calculated here should be considered as upper limits. Nevertheless, the FAGE HO_2 measurements represent clear evidence that the peroxy radicals observed at night during EASE 97 were not simply CH_3O_2 radicals remaining from daytime photochemistry [*cf. Monks et al.*, 1996].

OH measurements were made over the same two nights as HO_2 (1st-2nd and 21st-22nd May). On neither night were OH mixing ratios above the detection limit observed. Based on an averaging time of 15 min, the detection limit was estimated to be *ca* 2.5×10^5 molecules cm^{-3} (0.01 pptv) for a signal-to-noise ratio of 1; in effect, this represents an upper limit for $[\text{OH}]$ over these two nights.

Figure 3.9 Comparison of night-time PERCA $[\text{HO}_2+\text{RO}_2]$ and FAGE $[\text{HO}_2]$ data

(a) Night of 1st-2nd May, 1997

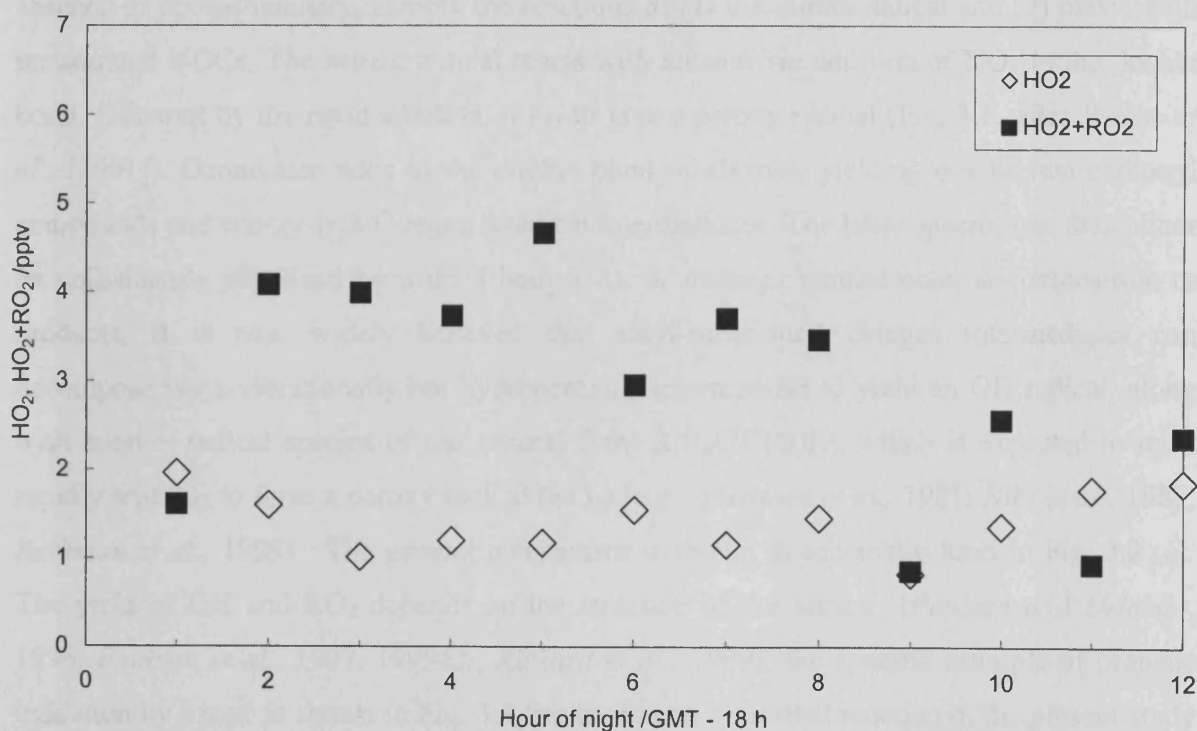
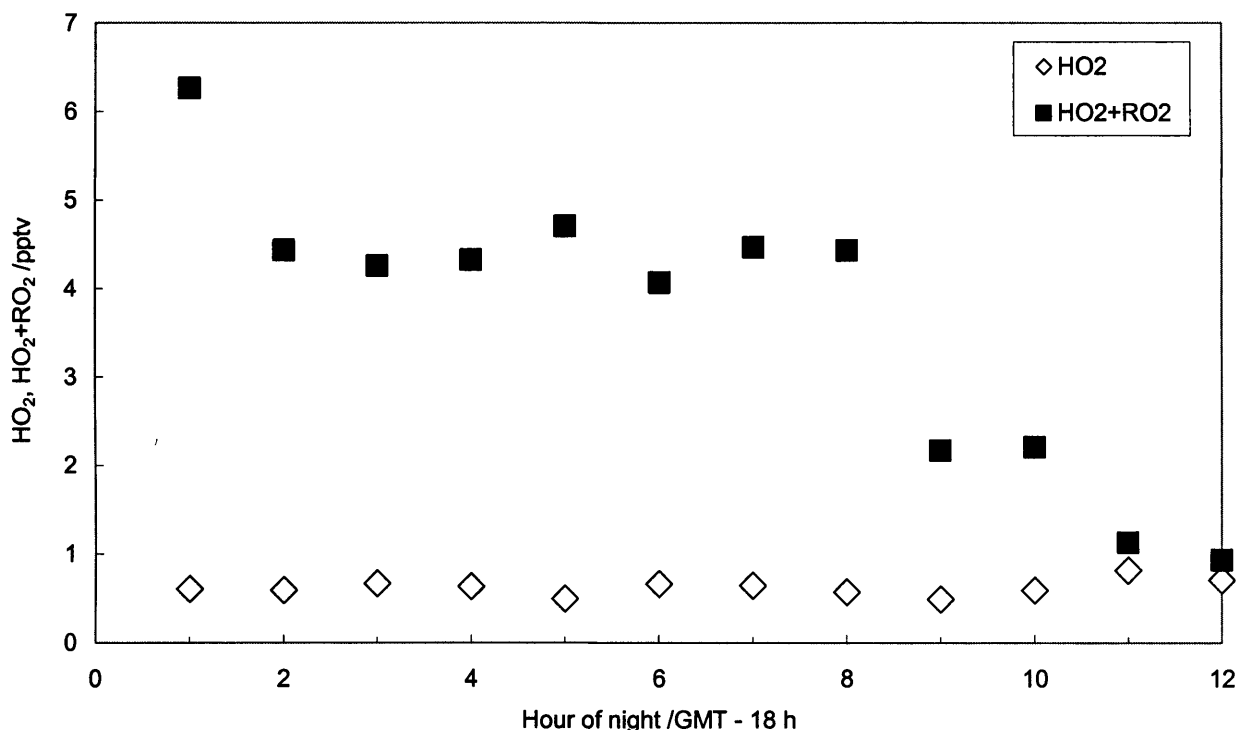


Fig. 3.9 *cont.*(b) Night of 21st-22nd May, 1997

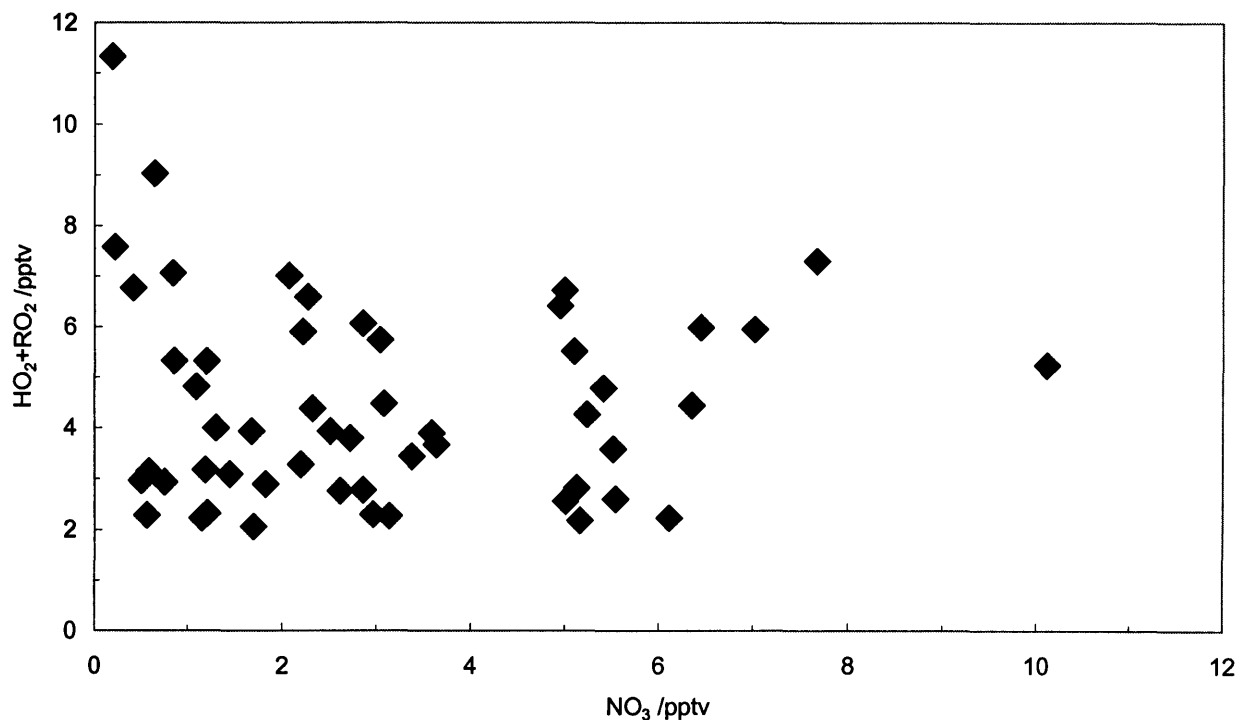
3.5 Peroxy Radical Production at Night during EASE 97

As outlined in Section 3.1, two mechanisms are known to produce peroxy radicals in the absence of photochemistry, namely the reactions of (1) the nitrate radical and (2) ozone with unsaturated VOCs. The nitrate radical reacts with alkenes *via* addition of NO₃ to the double bond, followed by the rapid addition of O₂ to give a peroxy radical (Fig. 3.1, after *Wayne et al.*, [1991]). Ozone also adds to the double bond of alkenes, yielding one or two carbonyl compounds and energy-rich Criegee biradical intermediates. The latter species can then either be collisionally stabilised by a third body (M), or undergo unimolecular decomposition to products. It is now widely believed that alkyl-substituted Criegee intermediates can decompose *via* a vibrationally hot hydroperoxide intermediate to yield an OH radical, along with another radical species of the general form R₁R₂C[•]C(O)R₃, which is expected to react rapidly with O₂ to form a peroxy radical (RO₂) [*e.g.*, *Martinez et al.*, 1981; *Niki et al.*, 1987; *Rathman et al.*, 1999]. The general mechanism is shown in schematic form in Fig. 3.2 (a). The yield of OH and RO₂ depends on the structure of the alkene [*Paulson and Orlando*, 1996; *Paulson et al.*, 1997, 1999a,b; *Rickard et al.*, 1999]; the specific example of propene oxidation by ozone is shown in Fig. 3.2 (b), as it is an important reaction in the present study

(Table 3.2). The major peroxy radical produced is likely to be $\text{HC(O)CH}_2\text{O}_2$ (pathway 1 in Fig. 3.2 (b)), which is expected to rapidly generate HO_2 in the presence of NO (reactions 3.2 and 3.5) [Paulson *et al.*, 1999b]. The OH produced in the ozone-alkene reactions will then react with a range of organic compounds to yield peroxy radicals, as during the day. The reactions of NO_3 and O_3 with alkanes and carbonyl compounds are relatively slow [Atkinson, 1994], and therefore unlikely to contribute significantly to the total peroxy radical production. However, the reactions of NO_3 with CH_4 and HCHO were considered in this work owing to the relatively high mixing ratios of these species in the troposphere.

Figure 3.10 shows a scatter plot of measured $[\text{HO}_2 + \text{RO}_2]$ versus $[\text{NO}_3]$, where each data point is a composite wind sector hour, with all sectors plotted together as one series. Clearly there is no significant correlation between the two variables ($r^2 = 0.002$). Similar results were obtained both by plotting all hourly data obtained during the campaign without sorting by wind sector, and by plotting each wind sector separately.

Figure 3.10 Scatter plot of $[\text{NO}_3]$ versus $[\text{HO}_2 + \text{RO}_2]$, using all hours where $[\text{NO}_3] \neq 0$, where all wind sectors are plotted as a single series



This result is in contrast with the measurements reported by Carslaw *et al.* [1997b], where a positive correlation was observed between $\text{HO}_2 + \text{RO}_2$ and NO_3 at the Weybourne Atmospheric Observatory in Norfolk. However, the lack of correlation is not surprising, given

that NO_3 is both a source [Wayne *et al.*, 1991] and sink [Mellouki *et al.*, 1993; Biggs *et al.*, 1994] of peroxy radicals. An analogous plot of all night-time $[\text{HO}_2]$ measurements *versus* $[\text{NO}_3]$ (not shown) also showed no significant correlation.

In order to ascertain the sources of the observed peroxy radicals, rates (Φ) were calculated for the reactions of NO_3 and O_3 with those alkenes (alk_i) measured during EASE 97, namely ethene, propene, 2-methylpropene, but-1-ene, *cis*- and *trans*-but-2-ene, *cis*- and *trans*-pent-2-ene, 1,3-butadiene and isoprene (Equations 3.19 and 3.20, respectively).

$$\Phi_{\text{NO}_3} = \sum_i^{\text{alk}} k_{\text{NO}_3+\text{alk}_i} [\text{NO}_3] [\text{alk}_i] \quad (3.19)$$

$$\Phi_{\text{O}_3} = \sum_i^{\text{alk}} k_{\text{O}_3+\text{alk}_i} [\text{O}_3] [\text{alk}_i] \quad (3.20)$$

The rate coefficients used in the NO_3 calculations were taken from Atkinson [1994]. Values for the pentenes were unavailable; averaged values were therefore calculated according to the procedure adopted by Jenkin *et al.* [1997]. The rate coefficients for the O_3 reactions were taken from Atkinson [1997] where available; the rate coefficients used for the pentenes were averages calculated after Jenkin *et al.* [1997]. Uncertainties in the total rates for each mechanism were estimated using the measurement uncertainties given in Section 3.2.2 and literature 1σ uncertainties for the rate coefficients [Atkinson 1991; 1994; 1997], where available. Uncertainties for the remaining rate coefficients were taken as averages of the published cases.

Figure 3.11 shows a correlation plot of the total rate through the NO_3 and O_3 reactions with alkenes *versus* the measured sum of peroxy radicals, $[\text{HO}_2 + \text{RO}_2]$, where the data for all wind sectors are plotted as a single series. The level of correlation ($r^2 = 0.54$) represents evidence that production of peroxy radicals *via* NO_3/O_3 reactions was important during EASE 97.

Table 3.6 gives the total mean rates (and 1σ uncertainties) for the two sets of reactions, (1) NO_3 +alkenes and (2) O_3 +alkenes at night during EASE 97, averaged by wind sector, and the mean percentage contribution of ozone reactions to alkene oxidation.

Figure 3.11 Scatter plot of the total night-time rate through the NO_3 , O_3 + alkene reactions versus $[\text{HO}_2 + \text{RO}_2]$, using all hours where $[\text{NO}_3] \neq 0$, where all wind sectors are plotted as a single series

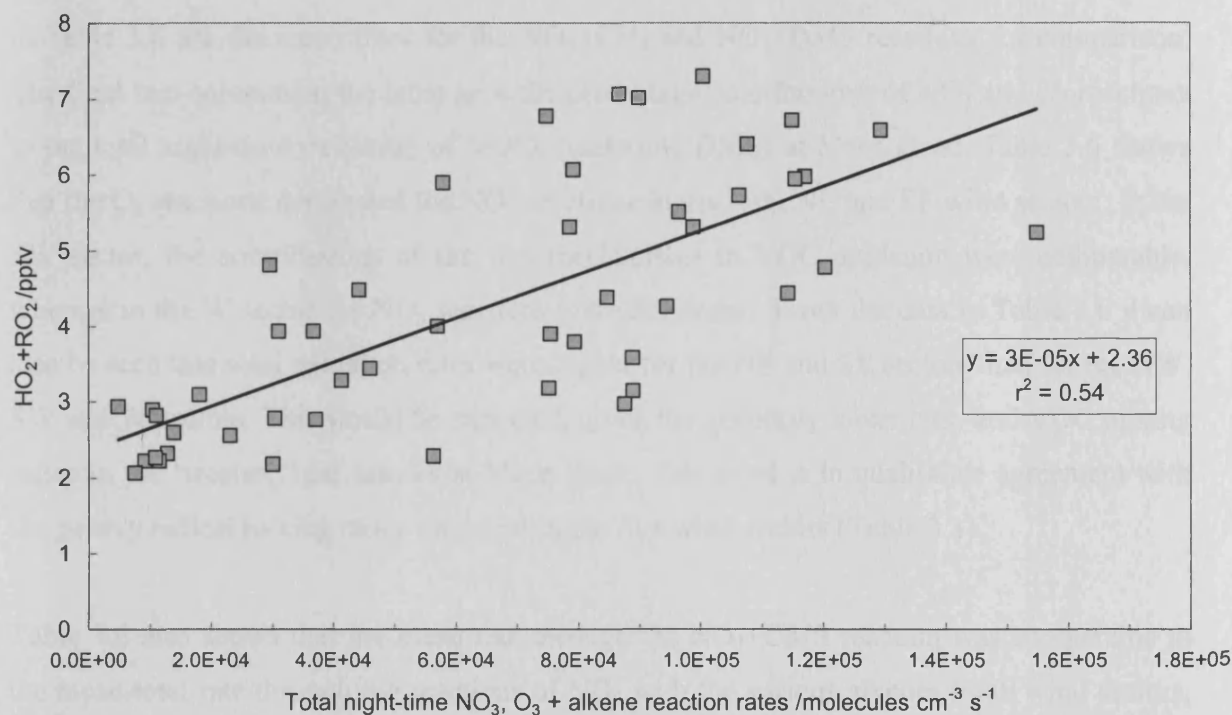


Table 3.6 Average night-time reaction rates by wind sector during EASE 97^a

Wind sector	$\text{NO}_3 + \text{CH}_4^b$	$\text{NO}_3 + \text{DMS}$	$\text{NO}_3 + \text{alkenes}$	$\text{O}_3 + \text{alkenes}$	O_3 contribution to alkene oxidation /%	Total VOC oxidation flux ^c	Contribution of NO_3 reactions /%	Contribution of O_3 reactions /%
NW	$(2.0 \pm 0.9) \times 10^3$	$(1.1 \pm 0.5) \times 10^4$	$(5.2 \pm 1.1) \times 10^3$	$(3.9 \pm 0.7) \times 10^4$	88.2	$(5.7 \pm 1.7) \times 10^4$	31.8	68.2
NE	$(3.2 \pm 1.4) \times 10^3$	$(1.4 \pm 0.6) \times 10^4$	$(1.7 \pm 0.4) \times 10^4$	$(6.8 \pm 1.0) \times 10^4$	80.0	$(1.0 \pm 0.3) \times 10^5$	33.5	66.5
SE	$(5.3 \pm 2.2) \times 10^3$	$(2.3 \pm 0.9) \times 10^4$	$(2.2 \pm 0.6) \times 10^4$	$(8.3 \pm 1.2) \times 10^4$	79.0	$(1.3 \pm 0.3) \times 10^5$	37.7	62.3
SW	$(3.0 \pm 1.3) \times 10^3$	$(2.6 \pm 1.1) \times 10^4$	$(1.1 \pm 0.2) \times 10^4$	$(3.9 \pm 0.7) \times 10^4$	78.0	$(7.9 \pm 2.0) \times 10^4$	50.6	49.4
W	$(3.8 \pm 1.8) \times 10^3$	$(2.4 \pm 1.2) \times 10^4$	$(6.5 \pm 1.8) \times 10^3$	$(2.0 \pm 0.4) \times 10^4$	75.5	$(5.4 \pm 1.3) \times 10^4$	63.2	36.8

^a All rates are in $\text{molecules cm}^{-3} \text{s}^{-1}$.

^b Upper limits using a maximum rate coefficient of $1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{s}^{-1}$ [Atkinson, 1994].

^c Includes DMS.

Table 3.6 shows that the ozone reactions dominated the night-time oxidation of alkenes over the whole data set (average contribution *ca* 80%). In terms of the overall oxidation of alkenes at Mace Head, the O_3 +alkene rates were significant, even when compared with daytime

OH+alkene oxidation rates: for example, the SE value of 8.3×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$ may be compared to an average daytime OH+alkene rate of 2.8×10^5 molecules $\text{cm}^{-3} \text{s}^{-1}$ (for integrated $[\text{OH}] = 1 \times 10^6$ molecules cm^{-3}). The 24-hour averages (assuming zero $[\text{OH}]$ at night; not shown in Table 3.6) were 1.1×10^5 and 1.5×10^5 molecules $\text{cm}^{-3} \text{s}^{-1}$, respectively. Also included in Table 3.6 are the mean rates for the $\text{NO}_3 + \text{CH}_4$ and $\text{NO}_3 + \text{DMS}$ reactions for comparison. The final two columns in the table give the percentage contributions of NO_3 and O_3 reactions to the total night-time oxidation of VOCs (including DMS) at Mace Head. Table 3.6 shows that the O_3 reactions dominated the NO_3 reactions in the NW, NE and SE wind sectors. In the SW sector, the contributions of the two mechanisms to VOC oxidation were comparable, whereas in the W sector the NO_3 reactions were dominant. From the data in Table 3.6 it can also be seen that total oxidation rates were higher for the NE and SE sectors than for the NW, SW and W sectors. This would be expected, given the generally lower NO_x and VOC mixing ratios in the 'westerly' air masses at Mace Head. This trend is in qualitative agreement with the peroxy radical mixing ratios observed in the five wind sectors (Table 3.1).

Table 3.6 also shows that the mean rate through the $\text{NO}_3 + \text{DMS}$ reaction was comparable to the mean total rate through the reactions of NO_3 with the various alkenes in all wind sectors, and significantly greater than that total for the NW, SW and W sectors, where $[\text{DMS}]$ was highest relative to VOC mixing ratios (see also Tables 3.1 and 3.2). The chemistry of NO_3 during EASE 97 is dealt with in full by *Allan et al.* [2000b], but these results show the importance of even small amounts of DMS in controlling NO_3 levels in the marine boundary layer [*Yvon et al.*, 1996; *Carslaw et al.*, 1997a,b; *Allan et al.*, 1999, 2000b]. The $\text{NO}_3 + \text{DMS}$ reaction alone accounted for *ca* 19, 14, 18, 33 and 44% of the total VOC oxidation at night in the NW, NE, SE, SW and W wind sectors, respectively. It is also interesting to compare the rate through the $\text{NO}_3 + \text{CH}_4$ and $\text{NO}_3 + \text{HCHO}$ reactions with the total rate through the $\text{NO}_3 + \text{VOC}$ reactions. The methane reaction (see Table 3.6) is seen to have been insignificant in the NE and SE sectors, but represented up to 11% of the $\text{NO}_3 + \text{VOC}$ oxidation rate in the three 'westerly' sectors, where mixing ratios of VOCs other than DMS were generally lower. The NO_3 reaction with HCHO (not shown in Table 3.6) was found to be relatively unimportant in all sectors, with a maximum rate of only 9.1×10^2 molecules $\text{cm}^{-3} \text{s}^{-1}$ (SE sector).

In order to assess the relative importance of peroxy radical production from NO_3 and O_3 reactions with alkenes, it was necessary to consider the reaction mechanisms in more detail. It

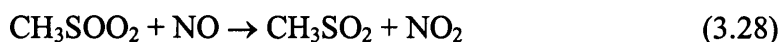
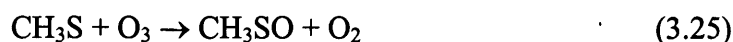
was assumed that each molecule of alkene (and CH₄) reacted with NO₃ yields one peroxy radical (see Fig. 3.1, after *Wayne et al.*, [1991]), *i.e.*,

$$P(\text{HO}_2 + \text{RO}_2)_{\text{NO}_3} = \Phi_{\text{NO}_3} \quad (3.21)$$

where P denotes the rate of production of radicals. The only exception to this is the NO₃ reaction with DMS, which yields the CH₃SCH₂O₂ peroxy radical initially. However, this species is not believed to be detectable by the PERCA technique, owing to the following sequence of reactions initiated by the high concentration of NO in the instrument inlet [*Balla et al.*, 1986; *Van Dingenen et al.*, 1994; *Carslaw et al.*, 1997b]:



In essence, the CH₃SCH₂O radical disproportionates rather than reacting with O₂ to yield HO₂, and therefore does not propagate the inlet chain reaction. However, other reactions of CH₃S are possible, which could lead to secondary formation of CH₃SOO₂, CH₃SO₂ and CH₃O₂ [*Cantrell et al.*, 1997b], which are detectable by the PERCA instrument:



Nevertheless, the reaction of CH₃S with NO [$k_{298} = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; *Balla et al.*, 1986, *DeMore et al.*, 1997] would be expected to predominate over the reactions with ozone [$k_{298} = 5.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; *DeMore et al.*, 1997] and NO₂ [$k_{298} = 6.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; *DeMore et al.*, 1997], given the conditions in the PERCA inlet, where [NO] is typically *ca* 3 ppmv (see Chapter 2), whereas ambient ozone was 30-40 ppbv and nitrogen dioxide a few ppbv at most during EASE 97 (see Table 3.1). During a measurement campaign at Weybourne, England, in 1994, *Carslaw et al.* [1997] measured an average [HO₂+RO₂] of

only 1.3 pptv on a night where the modelled $[\text{CH}_3\text{SCH}_2\text{O}_2]$ was almost 23 pptv. The $\text{NO}_3 + \text{DMS}$ reaction is therefore neglected in the following analysis.

As already mentioned, the yield of OH (and hence RO_2) from the reactions of ozone with alkenes varies according to the structure of the alkene [Paulson and Orlando, 1996; Paulson *et al.*, 1997, 1999a,b; Rickard *et al.*, 1999]. Table 3.7 shows the OH yields measured by various workers for the alkenes measured in EASE 97; the average values have been used in this study. Also included in Table 3.7 are the rate coefficients used for the reactions and their sources.

Table 3.7 Summary of OH yields and rate coefficients for the reaction of ozone with alkenes measured during EASE 97

Alkene	ATK	MARS	PAUL	NEEB	Mean	$k_{\text{ozone}}(298\text{K})^{\text{a}}/\times 10^{-18}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Ethene	0.12	0.14	0.18	—	0.15	1.59
Propene	0.33	0.32	0.35	0.34	0.34	10.1
<i>trans</i> -but-2-ene	0.64	0.54	0.64	—	0.61	190
But-1-ene	0.41	—	0.29	—	0.35	9.64
2-Methylpropene	0.84	0.60	0.72	0.60	0.69	11.3
<i>cis</i> -but-2-ene	0.41	0.33	0.37	—	0.37	125
1,3-butadiene	0.08	—	0.13	—	0.11	6.30
<i>trans</i> -pent-2-ene	—	—	0.47	—	0.47	160 ^b
<i>cis</i> -pent-2-ene	—	—	0.30	—	0.30	160 ^b
Isoprene	0.27	0.44	0.25	0.26	0.31	12.8

ATK Atkinson *et al.* [1992], Atkinson and Aschmann [1993]; MARS Marston and co-workers: McGill *et al.* [1999], Rickard *et al.* [1999]; PAUL Paulson *et al.* [1998, 1999a,b]; NEEB Neeb and Moortgat [1999].

^a Rate coefficients taken from Atkinson [1997] unless otherwise stated. ^b Estimated from Jenkin *et al.* [1997].

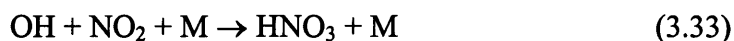
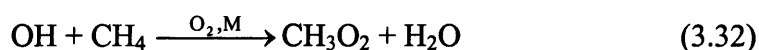
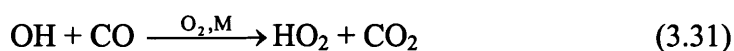
Since OH produces a second peroxy radical on reaction with the most abundant trace species, CO and CH_4 (as well as other VOCs), the effective peroxy radical yield is estimated to be twice the OH yield for each alkene, *i.e.*,

$$P(\text{HO}_2 + \text{RO}_2)_{\text{O}_3} = \sum_i^{\text{alk}} k_{\text{O}_3 + \text{alk}_i} [\text{O}_3] [\text{alk}_i] * 2Y_{\text{OH}_i} \quad (3.30)$$

where Y_{OH} represents the OH yield from a given O_3 -alkene reaction. Fig. 3.2 (b) shows the full reaction scheme for the reaction between ozone and propene, with estimated branching

ratios as given in *Atkinson* [1997], except for the stabilised Criegee biradical branching ratios [*Rickard et al.*, 1999]; the *syn*- and *anti*-CH₃CHOO* were assumed to be formed in equal amounts. Fig. 3.2 (b) shows that the calculation used in this work was a simplification, since OH and peroxy radicals may be produced *via* pathways not considered in Equation (3.30). The total HO₂+RO₂ yield estimated from Fig. 3.2 (b), assuming all OH formed goes on to react with CO or CH₄ to produce a peroxy radical, was *ca* 96%. Nevertheless, 69% of the total yield was estimated to be due to the decay of the *syn*-CH₃CHOO* Criegee biradical (species A in Fig. 3.2 (b)) *via* a vibrationally hot hydroperoxide (pathway 1 in Fig. 3.2 (b)). Hence Equation (3.30) may be taken to represent a reasonable lower limit for the peroxy radical yield for the ozone-propene reaction, and, by analogy, the other ozone-alkene reactions considered here. Other possible routes to peroxy radicals have not been considered further in the calculations presented in this chapter.

The assumption that all OH radicals formed in the reactions of ozone with alkenes reacted further to produce peroxy radicals was examined by calculating reactivity indices for the major loss reactions of OH. The reactions considered were:



VOCs other than methane were not included in this simple analysis. Equation (3.34) was then used to estimate a lower limit for the fraction of OH radicals reacting to form peroxy radicals, rather than non-radical products:

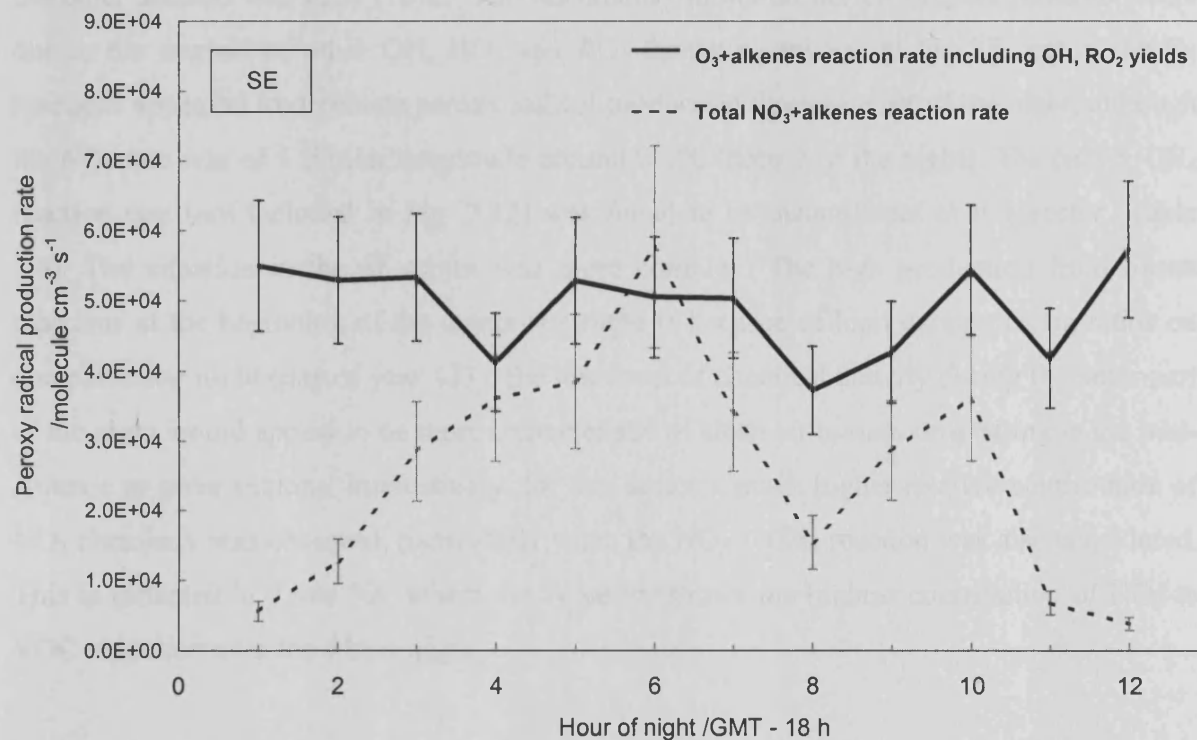
$$\text{Fractional peroxy radical production} = \frac{k_{31}[\text{CO}] + k_{32}[\text{CH}_4]}{k_{31}[\text{CO}] + k_{32}[\text{CH}_4] + k_{33}[\text{NO}_2]} \quad (3.34)$$

The average fractions obtained from Equation (3.34) were 0.97, 0.95, 0.85, 0.96 and 0.97 for the NW, NE, SE, SW and W wind sectors, respectively. The mean for the entire data set was 0.94.

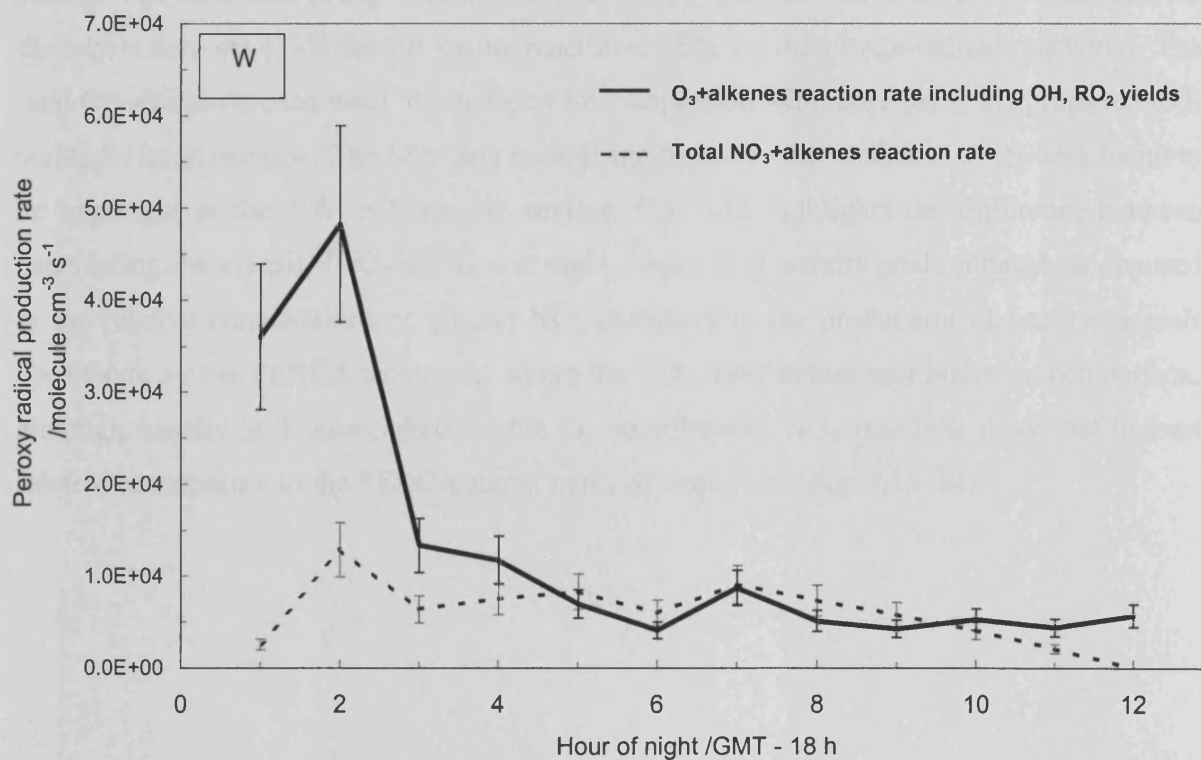
Figure 3.12 shows the estimated peroxy radical production rates (Equations 3.21 and 3.30) from alkene reactions for (a) the SE sector and (b) the W sector. The error bars in Fig. 3.12 represent 1σ confidence limits based on the uncertainties in the total reaction rates, as well as

Figure 3.12 Estimated night-time peroxy radical production rates from the NO_3 +alkene and O_3 +alkene reactions during EASE 97^a

(a) SE wind sector



(b) W wind sector



^a The total rates are given for the NO_3 reactions, since one RO_2 is assumed to be formed from each reaction, whereas literature values of OH (and hence RO_2) yields are factored into the O_3 reaction rates. The error bars are estimated 1σ uncertainties.

the estimated error limits in the OH yields (Table 3.7). Since there is a range of OH yields reported in the literature, the uncertainty in OH yield for each ozone-alkene reaction was estimated to be the standard deviation of the measured values given in Table 3.7. For the pentenes, where only one value of the OH yield has been reported, the mean uncertainty for the other alkenes was used (18%). The uncertainty limits do not encompass possible errors due to the neglect of other OH, HO₂ and RO₂ formation routes. In the SE sector, the O₃ reactions appeared to dominate peroxy radical production through most of the night, although the NO₃ rate was of a similar magnitude around 01:00 (hour 7 of the night). The NO₃ + CH₄ reaction rate (not included in Fig. 3.12) was found to be insignificant in this sector (Table 3.6). The situation in the W sector was more complex. The high production from ozone reactions at the beginning of the composite night is because of high ozone mixing ratios on one particular night (day of year 137): the low level of chemical activity during the latter part of the night would appear to be more characteristic of clean air masses originating in the mid-Atlantic or polar regions. Interestingly, for this sector a much higher relative contribution of NO₃ chemistry was observed, particularly when the NO₃ + CH₄ reaction was also considered. This is reflected in Table 3.6, where the W sector shows the highest contribution of NO₃ to VOC oxidation over the whole night.

Figure 3.13 summarises the estimated mean peroxy radical production rates for the five wind sectors. The error bars in Fig. 3.13 represent mean 1σ uncertainties in the production rates for the whole data set (19% for the ozone reactions; 25% for the nitrate-radical reactions). The total O₃+alkene reaction rates are included for comparison with those using the projected RO₂ yields for each reaction. The NO₃ data include the reaction with methane, which was found to be important in the NW, SW and W sectors. Fig. 3.13 highlights the difference between considering the overall VOC oxidation at night, where O₃ generally predominated, as opposed to the relative contributions of O₃ and NO₃ chemistry to the production of peroxy radicals observable by the PERCA technique, where the NO₃ contribution was higher in comparison, although usually still outweighed by the O₃ contribution. NO₃ reactions made the highest relative contribution to the PERCA signal in the W sector (see Fig. 3.12 (b)).

Figure 3.13 Bar chart showing the average VOC reaction rates and estimated peroxy radical production rates for each wind sector: (1) the total NO_3 +alkene, CH_4 reaction rate; (2) the total O_3 + alkene reaction rate, for comparison; (3) the O_3 + alkene rate, taking into account OH (and hence RO_2) yields

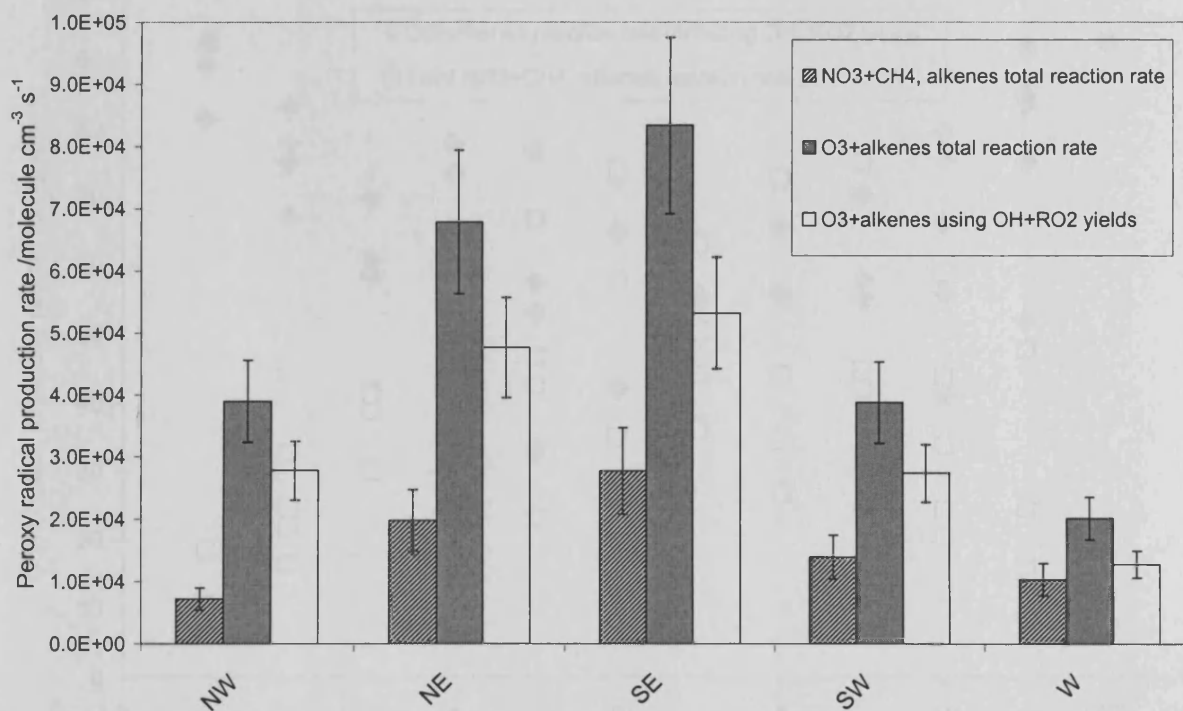
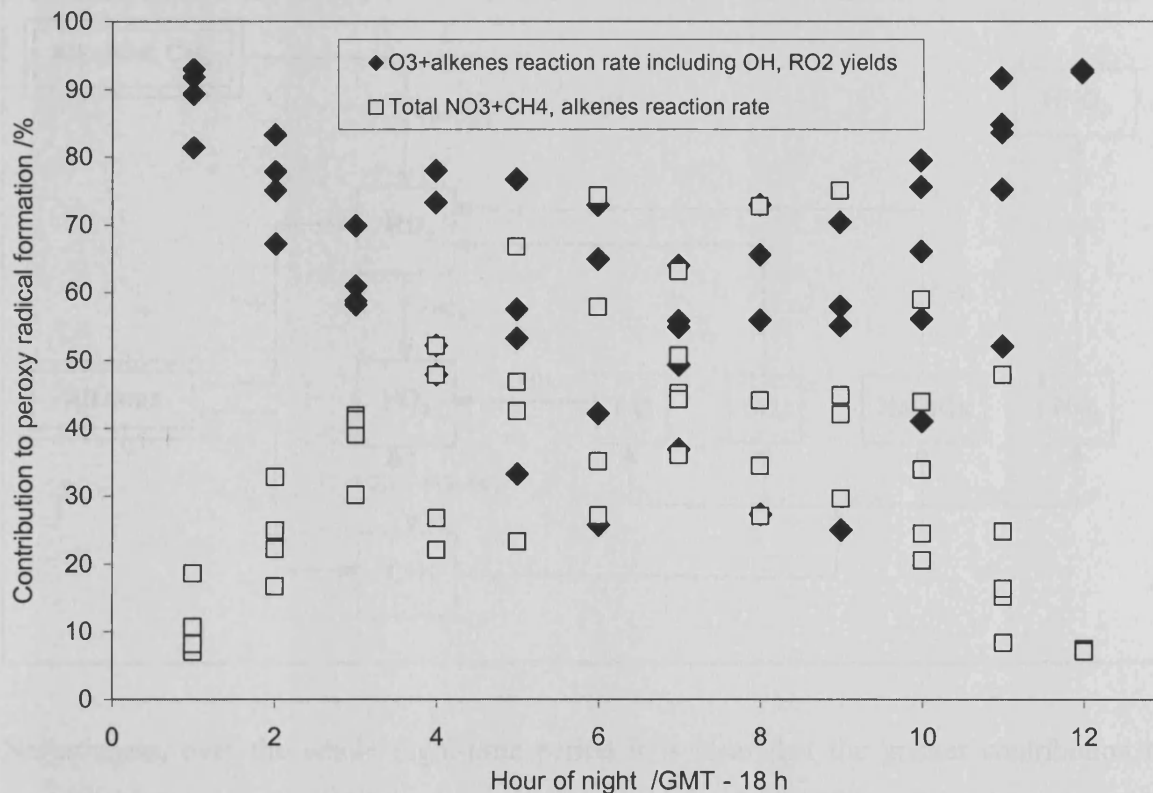


Figure 3.14 shows the estimated percentage contributions to the PERCA signal throughout the night for all wind sectors. Fig. 3.14 (a) shows the values for each wind sector, whilst Fig. 3.14 (b) shows the overall average contributions by hour. Fig. 3.14 indicates that the O_3 contribution was always at least equal to that of NO_3 , and generally greater, apart from in the middle of the night, when NO_3 mixing ratios were highest. It is worth noting that the two sets of reactions contributed almost equally to the PERCA signal in the central portion of the night, since previous studies have tended to conclude that either NO_3 or O_3 reactions are dominant (see Figure 3.15).

Figure 3.14 Estimated percentage contributions of NO_3 reactions and O_3 reactions to peroxy radical formation at night during EASE 97

(a) All wind sectors plotted as individual points



(b) Averages over all wind sectors

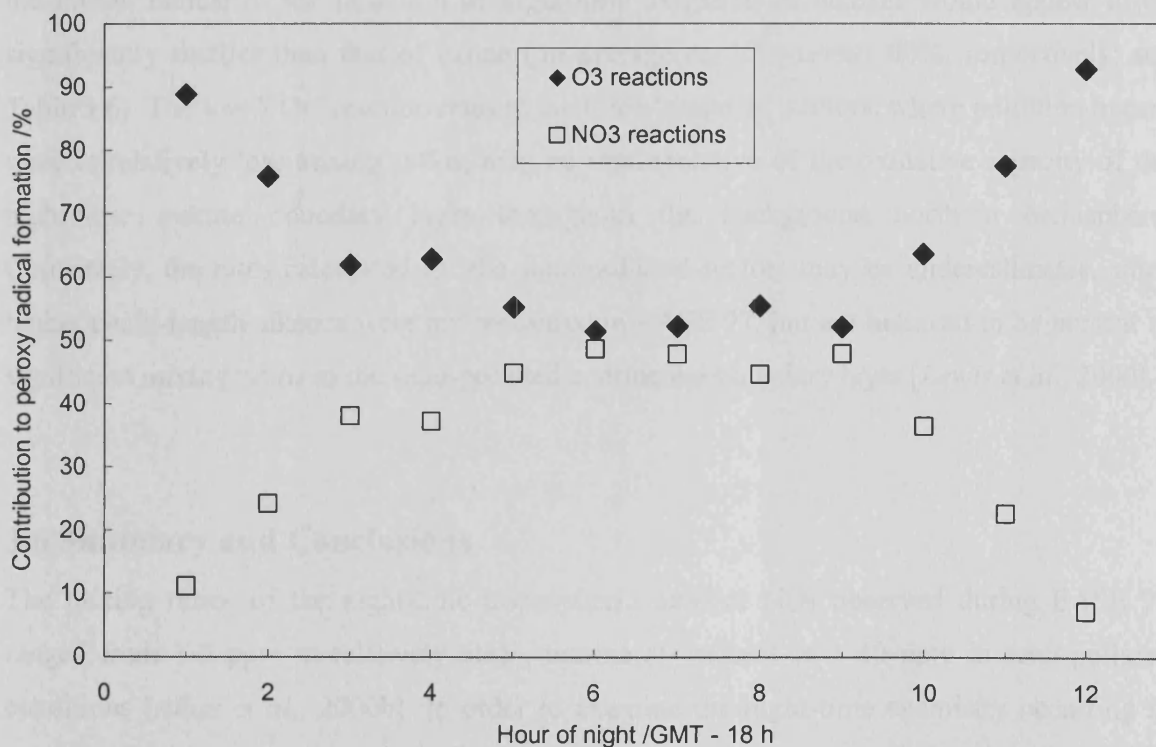
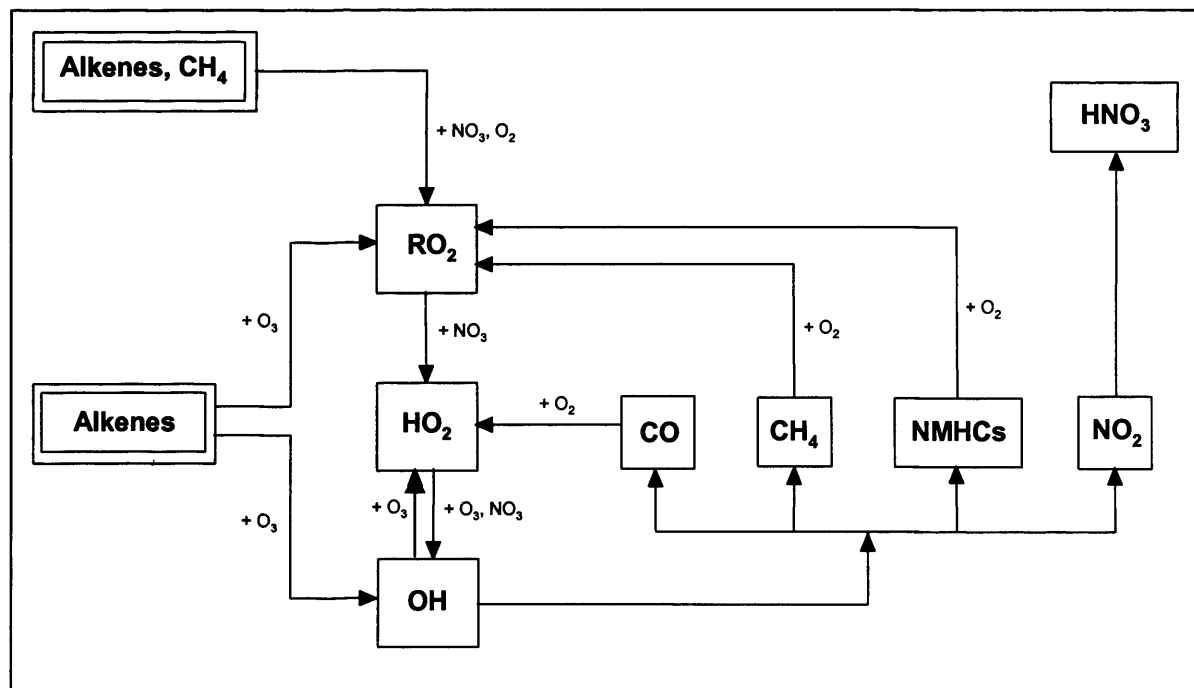


Figure 3.15 Schematic representation of night-time radical initiation and propagation chemistry. The scheme excludes all radical-radical self- and cross-reaction termination processes



Nevertheless, over the whole night-time period it is clear that the greater contribution to production of the peroxy radicals observed at night during EASE 97 was from the reactions of ozone with alkenes (*ca* 66% on average over the whole data set). Certainly the contribution of the nitrate radical to the initiation of night-time oxidation of alkenes would appear to be significantly smaller than that of ozone (on average *ca* 20% *versus* 80%, respectively; see Table 3.6). The low VOC reaction rates in the three ‘westerly’ sectors, where pollution tracers were at relatively low mixing ratios, may be representative of the oxidative capacity of the night-time marine boundary layer throughout the background northern hemisphere. Conversely, the rates calculated for the semi-polluted sectors may be underestimates, since higher chain-length alkenes were not measured in EASE 97, but are believed to be present in significant mixing ratios in the semi-polluted continental boundary layer [Lewis *et al.*, 2000].

3.6 Summary and Conclusions

The mixing ratios of the night-time tropospheric oxidant NO_3 observed during EASE 97 ranged from 1-5 pptv in relatively clean, marine air masses to 1-40 pptv in semi-polluted conditions [Allan *et al.*, 2000b]. In order to examine the night-time chemistry occurring in

differing air masses observed at Mace Head during the campaign, the data from EASE 97 were divided up into five wind sectors according to incident wind direction: north-easterly (NE), 0-90°; south-easterly (SE), 90-200°; south-westerly (SW), 200-250°; westerly (W), 250-300°; and north-westerly (NW), 300-360°, as shown in Fig. 3.3. The average rate of NO₃ production ($P(\text{NO}_3) = k_1[\text{NO}_2][\text{O}_3]$) was much higher at night in the relatively polluted SE wind sector, where [NO₂] was highest, than any of the other sectors. A positive correlation between $P(\text{NO}_3)$ and [NO₃] was evident in the data classified by wind sector, particularly in the maximum [NO₃] observed in each wind sector, which indicated the presence of significant direct removal processes of the nitrate radical [Heintz *et al.*, 1996; Allan *et al.*, 1999]. The longest NO₃ turnover lifetimes were observed in the three, relatively clean ‘westerly’ wind sectors, NW, SW and W (10.7, 31.9 and 22.1 min, respectively). A clear anti-correlation between both NO₃ and its turnover lifetime and [NO] was observed, suggesting that NO was a controlling influence on [NO₃] in the EASE 97 campaign, although other loss processes, particularly the NO₃+DMS and NO₃+alkene reactions (Tables 3.1 and 3.2), were also likely to have been important (see later) over the range of atmospheric conditions sampled, as noted previously by Allan *et al.* [2000b].

No correlation was observed between either [HO₂+RO₂] or [HO₂] alone with [NO₃], which underlines the fact that peroxy radicals are both formed by NO₃ reactions [Wayne *et al.*, 1991] and destroyed by reaction with NO₃ [e.g., Mellouki *et al.*, 1993]. This result is in contrast with Mihelcic *et al.* [1993], who observed a negative correlation between [HO₂+RO₂] and [NO₃] at Schauinsland in Germany, and Carslaw *et al.* [1997b], who observed a positive correlation between [HO₂+RO₂] and [NO₃] at Weybourne, on the East coast of England.

The sustained mixing ratios of peroxy radicals observed at night (net decay rates of <0.5 pptv h⁻¹ in all wind sectors) demonstrated a requirement for substantial radical production processes, in the absence of daytime photochemistry. In support of this finding, the average modelled lifetimes of HO₂ and RO₂ (where CH₃O₂ was taken to represent all RO₂ present) were all less than 1 h and 3 h, respectively, even with [NO] set to zero. When NO₃ was removed from the models, the lifetime of CH₃O₂ became considerably longer (>4 h). This points to the importance of the nitrate radical in the processing of RO₂ at night in the absence of NO (*cf.* reactions 3.2 and 3.3). This route to HO₂, and hence OH at night, is likely to be of importance in the night-time troposphere, whatever the original source of RO₂ (see Fig. 3.15). Measurements of OH and HO₂ on two nights using the FAGE technique gave an upper limit

for [OH] of 2.5×10^5 molecules cm^{-3} and an average $[\text{HO}_2]/[\text{HO}_2 + \text{RO}_2]$ ratio of 0.27 (upper limit).

In order to assess the relative contributions of ozone and NO_3 reactions to the peroxy radical signal observed at night during EASE 97, reaction rate calculations were performed in two stages. First, the total reaction rates were calculated for each mechanism. This showed that the ozone-initiated oxidation routes of VOCs outweighed those of NO_3 in the NW, NE and SE wind sectors. However, in the SW sector the two mechanisms operated at similar rates on average, and oxidation by NO_3 was the dominant route in the W sector. The oxidation of alkenes at night by ozone was greater by a factor of four than that by NO_3 over the whole data set. Next, peroxy radical formation rates were estimated from both reaction mechanisms (Figs 3.1 and 3.2). In the NO_3 case, it was assumed that one RO_2 was formed from each $\text{NO}_3 + \text{alkene}$ reaction [Wayne *et al.*, 1991]. The $\text{NO}_3 + \text{CH}_4$ and $\text{NO}_3 + \text{HCHO}$ reactions were also considered, but not that with DMS, since the main product of this reaction is $\text{CH}_3\text{SCH}_2\text{O}_2$, which is not believed to be detectable by the PERCA technique. In the O_3 case, literature values of OH (and inferred RO_2) yields were used to estimate total RO_2 production. The calculations showed that ozone reactions produced more peroxy radicals over the whole night-time period (defined as where $[\text{NO}_3] \neq 0$) than nitrate reactions (66 *versus* 34%, on average). However, the two mechanisms were found to operate at a similar rate in the middle of the night, when $[\text{NO}_3]$ was highest. The main importance of these results is perhaps that there was a significant contribution from both mechanisms (see Fig. 3.15), since previous studies have tended to emphasise one as dominant over the other. The VOC oxidation rates from the three 'westerly' sectors, where tracer mixing ratios were relatively low, may be representative of the night-time oxidative capacity of the marine boundary layer throughout the background northern hemisphere. Conversely, the rates calculated for the semi-polluted sectors may be underestimates, since higher chain-length alkenes were not measured in EASE 97, but are believed to be present in significant mixing ratios in the semi-polluted continental boundary layer [e.g., Lewis, 2000; Lewis *et al.*, 2000].

Chapter 4 – A seasonal comparison of ozone photochemistry at Mace Head, Ireland

4.1 Introduction

4.1.1 Ozone photochemistry in the troposphere

As discussed in Chapter 1, the role of *in-situ* photochemistry in the tropospheric ozone budget has become an important research topic in atmospheric chemistry in recent years. A distinct annual cycle in ozone mixing ratios, with a broad maximum in the spring and a minimum in the summer, has been reported in a number of different locations in both the boundary layer and the free troposphere in the Northern Hemisphere [*e.g.*, Derwent *et al.*, 1998; Monks, 2000, and references therein]. In contrast, winter maxima of many pollution tracers, including NO_x (NO+NO₂), carbon monoxide (CO), methane (CH₄) and non-methane hydrocarbons (NMHCs), have been observed at remote sites in northern Europe [*e.g.*, Hov and Stordal, 1992; Novelli *et al.*, 1994]. It is possible that the increase in photochemical activity in early spring, coupled with the build-up of relatively high levels of ozone precursors in the winter months, leads to high photochemical ozone production in spring, and hence makes an important contribution to the observed spring ozone maximum [*e.g.*, Penkett *et al.*, 1993; Derwent *et al.*, 1998].

Ozone production in the troposphere is a non-linear process, requiring both NO_x and volatile organic compounds (VOCs). In a recent review of the results from ground-based field campaigns designed to investigate tropospheric ozone photochemistry, Solomon *et al.* [2000] concluded that in most rural areas in both North America and Europe, ozone production is NO_x-limited. Conversely, in urban areas, where [NO_x] is generally high (>1-2 ppbv), ozone production is generally VOC-limited. Ozone control strategies, therefore, rely on accurate knowledge of precursor mixing ratios both in urban plumes and in rural areas downwind of urban pollution centres, as well as reliable indicators of NO_x- and VOC-limitation.

The aim of this chapter is to compare and contrast the ozone photochemistry observed during two field campaigns carried out at Mace Head, on the Atlantic coast of Ireland: the Atmospheric Chemistry in the Oceanic Environment (ACSOE) Eastern Atlantic Summer/Spring Experiments in summer (July-August) 1996 (EASE 96) and spring (April-

May) 1997 (EASE 97). The Mace Head Atmospheric Research Station has already been introduced in Chapter 3, which presents a study of the night-time chemistry during EASE 97.

4.1.2 Measurements during EASE 96 and EASE 97

A summary of the measurements undertaken during the two campaigns and their respective instrument operators is given in Table 4.1. Table 4.1 does not represent an exhaustive list of measurements obtained during either campaign, but rather concentrates on those which have been used in the course of this work.

4.2 Data Analysis – Air Mass Classifications

4.2.1 Data classification method

In order to examine the chemistry occurring in differing air masses observed at Mace Head during the ACSOE Mace Head campaigns, the data from EASE 96 and 97 were divided up according to incident wind direction at the site. Previous work at Mace Head has shown that the station regularly receives relatively clean air masses from southerly latitudes, the mid-Atlantic and the Arctic, as well as more polluted air masses advected from Britain and continental Europe [Simmonds *et al.*, 1997]. Five wind sectors were chosen for analysis, as shown in Figure 3.3 (Chapter 3): north-easterly (NE), 0-90°; south-easterly (SE), 90-200°; south-westerly (SW), 200-250°; westerly (W), 250-300°; and north-westerly (NW), 300-360°. The effects of local sea/coast breezes were removed from the analysis by selecting data only where the local wind speed was over 3 m s^{-1} [*cf. Cape et al.*, 2000].

Two methods of allocating data to wind sectors were employed. Where available, minute-averaged data were allocated directly to a particular wind sector, based on the measured wind direction and speed during that minute. Averaging of these data for each minute of the day enabled composite diel cycles of many tracers, containing up to 1440 data points, to be compiled for each sector. Secondly, hourly averages of all measurements were calculated for both campaigns. The hourly averaged data points were then allocated to a wind sector if the wind-direction indicated 45 or more minutes' worth of data (75%+) within that sector for a given hour. Hours in which there was no dominant sector by this criterion were rejected. The selected data points were then used to derive hourly averaged diel cycles over both campaigns for each wind sector (*i.e.*, 24 averaged data points for each variable per sector). This second, hourly averaging method was employed in the analysis of the night-time EASE 97 data

Table 4.1 Measurements undertaken during EASE 96 and EASE 97^a

Species/Quantity	Technique	Organisation ^b
OH	FAGE	1
Peroxy radicals	FAGE [HO ₂], PERCA [HO ₂ +RO ₂]	1, 2
Photolysis frequencies $j(\text{O}^1\text{D})$ and $j(\text{NO}_2)$	Filter radiometry	1, 2, 3
Meteorological data (wind speed, wind direction, water vapour concentration)	Automated weather station; IR (H ₂ O)	1,3
O ₃	UV (Monitor Labs 8810)	4
NO ^c	Custom-built NO/O ₃ chemiluminescence detection system	5
NO ₂ ^c	As above, with photochemical NO ₂ → NO conversion; also DOAS	5
NO _y ^c	As above, with gold tube/CO NO _y → NO conversion	5
NO, NO ₂ , NO _y	Techniques as above; CRANOX (Ecophysics)	5
CO, CH ₄	GLC-ECD-FID	4+6
HOOH, ROOH ^d	Dual-channel fluorimetric detector	5
HCHO	Fluorimetric detector based upon Hantzsch reaction; TDLAS ^e	5, 7 ^e
VOCs, including DMS	High-frequency automated GC	1
Condensation nuclei (particles >3nm, >10 nm)	CPC Particle Counters 3022, 3025	8
Nitrate radical, NO ₃	DOAS (Differential Optical Absorption Spectroscopy)	5

^a Unless otherwise indicated, measurements of each species were undertaken during both campaigns.

^b 1 University of Leeds, UK; 2 University of Leicester, UK; 3 Institute for Terrestrial Ecology, Penicuik, Midlothian, UK; 4 Mace Head Atmospheric Research Station, Galway, Ireland; 5 University of East Anglia, UK; 6 University of Bristol, UK; 7 Imperial College, London, UK; 8 University of Birmingham, UK.

^c A few days of measurements only during EASE 96.

^d Total peroxides only during EASE 96.

^e EASE 96 only.

(Chapter 3), as many of the salient measurements were only available at a time resolution approaching 1 h.

4.2.2 Comparison of the wind sector analysis with other data classification methods

Other participants in the ACSOE EASE campaigns utilised different air mass classification methods for data analysis, in particular based solely or in part on wind trajectory analysis. It is instructive to compare the results of the Leicester (ULi) analysis, using only local wind direction and wind speed, with the more complex data allocation schemes developed at the University of Leeds [ULe; *Carslaw et al.* 1999a,b; 2000; 2001a,b] and the Institute of Terrestrial Ecology [ITE; *Cape et al.*, 2000].

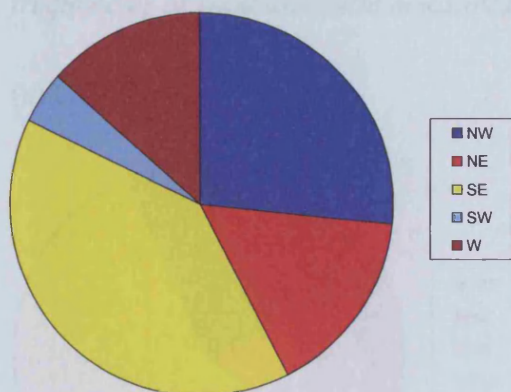
Comparison with University of Leeds air mass classifications

The ULe data classification method for the EASE campaigns was based on the European Centre for Medium Range Weather Forecasting (ECMWF) five-day back trajectories calculated at six hourly intervals throughout both campaign periods, in conjunction with NMHC measurements [*Carslaw et al.* 1999a,b; 2000; 2001a,b; *Lewis et al.*, 1997, 1999]. The arrival point for the trajectories was set at 53°19'34"N; 9°54'14"W, with an arrival pressure of 1000 mb [*Lewis et al.*, 1999]; the output data available from the ECMWF consisted of latitude, longitude and pressure of the trajectory at 30 min intervals for the five days prior to arrival of the air mass at Mace Head. For EASE 96, three significant air mass types were identified according to the ULe method: *Anti-cyclonic* easterly, associated with relatively polluted air which had passed over the UK prior to arrival in western Ireland; *Tropical Maritime*, associated with clean air masses from southerly latitudes; and *Westerly*, associated with clean air masses from the mid-Atlantic, often advected all the way from the USA. For EASE 97, where airflows from the westerly and south-westerly sectors were seldom encountered[†], a different set of air masses was identified for analysis: *UK* anticyclonic, as in EASE 96; *France* anti-cyclonic, where air was advected from the north-west, passing over northern England/southern Scotland and then north-west Europe (in particular, France), before turning north-west again to the south of England, and finally advected to Mace Head from a south-easterly direction; and *Polar*, associated with relatively unpolluted air from northerly latitudes. The periods associated with each air mass type are detailed by *Carslaw et al.* [1999a; 2001a] and *Lewis et al.* [1997; 1999].

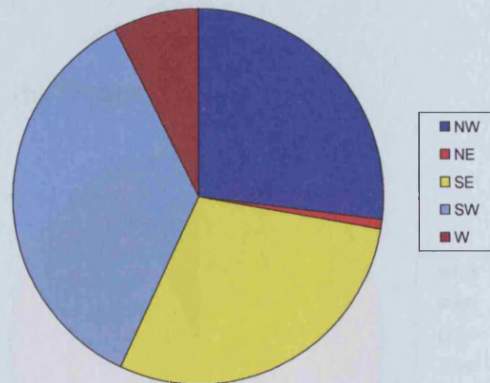
[†] A clean-air, 'westerly' period was observed at the beginning of EASE 97 [*Lewis et al.*, 1999], which fell largely before the beginning of the PERCA measurements, and is therefore not considered in this comparison.

Figure 4.1 University of Leeds air mass classifications for EASE 96 in terms of relative frequencies of wind direction measured at Mace Head

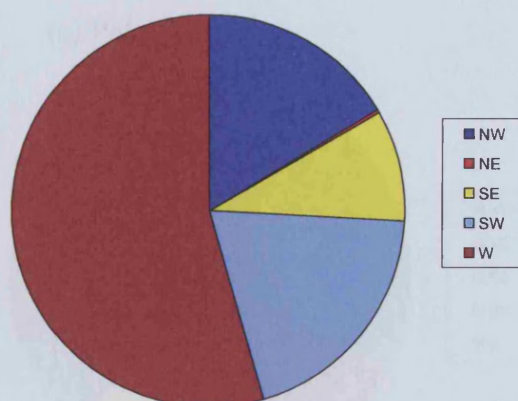
(a) Anti-cyclonic (UK)



(b) Tropical Maritime



(c) Westerly

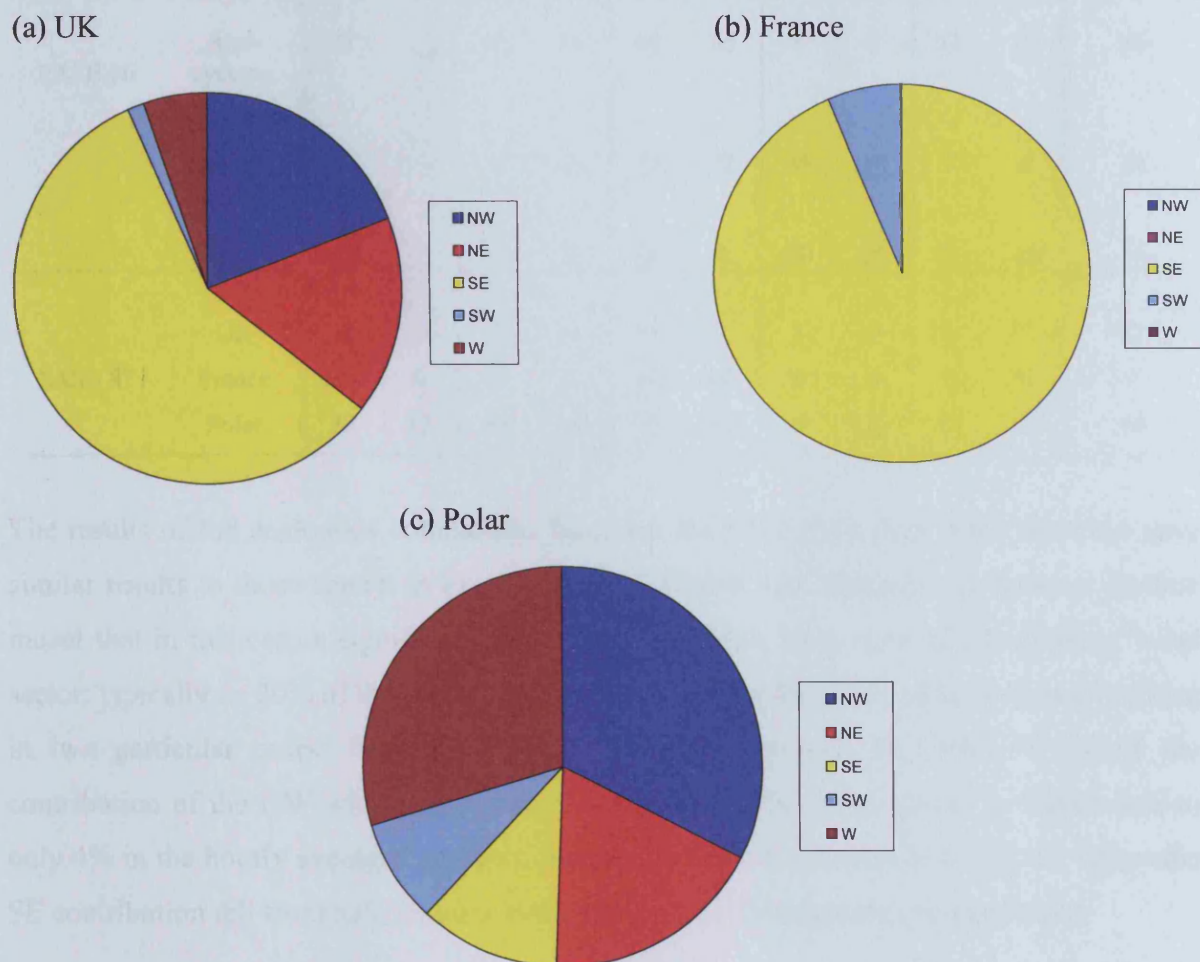


Using the minute averaged wind sector data to classify each of the ULe air masses, the relative frequencies shown in Figure 4.1 were obtained, where the panels represent (a) Anti-cyclonic, (b) Tropical Maritime, and (c) Westerly air masses, respectively. The analogous results for the three ULe air masses analysed in EASE 97 (UK, France and Polar) are shown in Figure 4.2. The results from Figs 4.1 and 4.2 are summarised in Table 4.2, together with the equivalent results based on the hourly averaged wind direction allocations (see Section 4.2.1).

Fig. 4.1 (a) shows that in EASE 96, the semi-polluted, anti-cyclonic (UK) air mass identified by Leeds comprised contributions from all five ULi wind sectors, although the SE and the NE

wind directions together made up over 50% of the total. Panels (b) and (c) of Fig. 4.1 show that both the Tropical Maritime and Westerly air mass types were dominated by the three

Figure 4.2 University of Leeds air mass classifications for EASE 97 in terms of relative frequencies of wind direction measured at Mace Head



‘westerly’ sectors (SW, W and NW); this effect was particularly marked for the Westerly air mass, where the NE and SE sectors together only contributed <10% to the total. The single most important wind directions were, as would be expected, SW for the Tropical Maritime and W for the Westerly air masses.

Panels (a) and (b) of Fig. 4.2 indicate that both the UK and France anti-cyclonic air masses identified by Leeds for EASE 97 were dominated by winds from the SE sector, as measured at Mace Head. In contrast, Fig. 4.2 (c) shows that the Leeds Polar air mass classification comprised mainly SW, W and NW winds at Mace Head (70%).

Table 4.2 University of Leeds air mass classifications for EASE 96 and EASE 97 in terms of percentage contribution of each wind direction measured at Mace Head: minute averaged and hourly averaged data

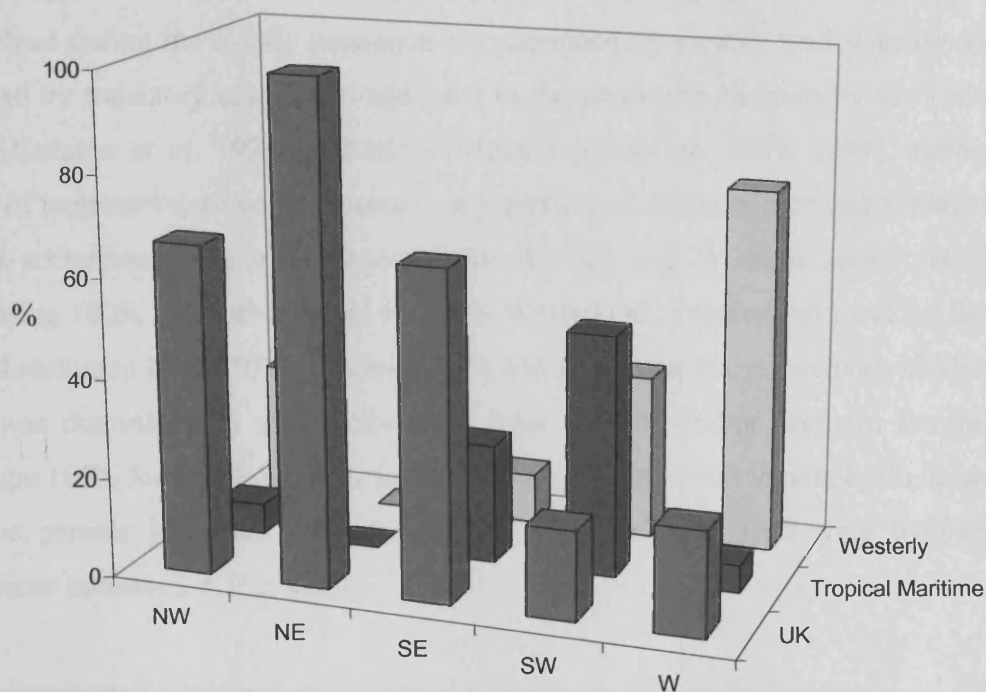
Campaign	ULe air mass	NW		NE		SE		SW		W		Undefined
		min	hour	min	hour	min	hour	min	hour	min	hour	hour
EASE 96	Anti-cyclonic (UK)	27	18	16	14	40	35	4	5	13	10	18
	Tropical maritime	27	4	1	0	29	32	36	40	7	6	18
	Westerly	16	11	0	0	9	8	20	15	55	48	18
EASE 97	UK	19	13	16	14	58	33	1	2	6	7	31
	France	0	0	0	0	94	90	6	4	0	0	6
	Polar	32	19	19	19	11	24	8	5	30	19	14

The results of the analogous comparison based on the hourly averaged wind direction gave similar results to those shown in Figs 4.1 and 4.2 (Table 4.2), although the analysis method meant that in this case a significant proportion of the data were rejected ('Undefined' wind sector; typically *ca* 20% of the total number of hours per sector). This effect was most striking in two particular cases: first, the Tropical Maritime air mass in EASE 96, where the contribution of the NW wind sector was reduced from 27% in the minute averaged data to only 4% in the hourly averaged analysis; second, for the UK air mass in EASE 97, where the SE contribution fell from 58% (minute averaged data) to 33% (hourly averaged data).

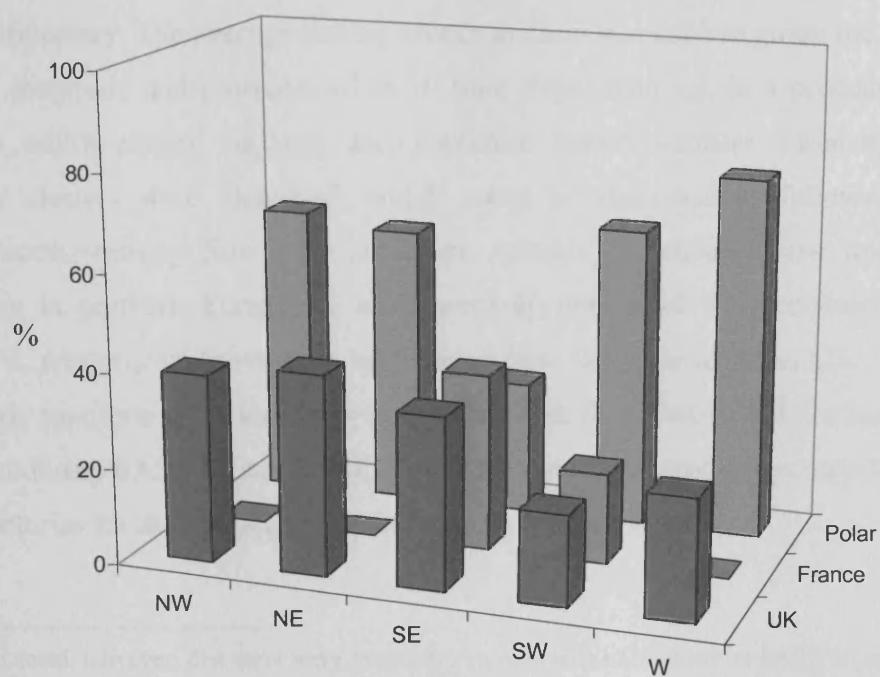
The results of the reverse comparison, where the percentage contributions of a given ULe air mass classification to each wind sector were calculated, are presented in Figure 4.3 (hourly averaged data); periods not allocated by Leeds to any air mass were not included in this analysis. Fig. 4.3 (a) shows that in EASE 96, the NE, SE and NW wind sectors all comprised mostly semi-polluted air from UK anti-cyclonic air masses, whereas the SW and W sectors mainly comprised relatively clean Tropical Maritime and Westerly air (total contributions 82% and 79%, respectively). The W wind sector was the best-defined clean sector, comprising 73% Westerly air. For EASE 97, Fig. 4.3 (b) shows that the NW and NE sectors both comprised a relatively even mixture of semi-polluted air (UK air mass) and 'clean' air

Figure 4.3 Percentage contributions of University of Leeds air mass classifications to each University of Leicester wind sector

(a) EASE 96



(b) EASE 97



(Polar air mass). The SE wind sector comprised mainly anti-cyclonic air (UK and France air masses), whereas the W and SW sectors were both dominated by relatively clean air advected from the Arctic (Polar air mass).

In summary, the wind sectors chosen for analysis based purely on wind direction measured at Mace Head during the EASE campaigns corresponded reasonably well with the air masses identified by trajectory calculation and used in the published analyses by the University of Leeds [*Carslaw et al.* 1999a,b; 2000; 2001a,b; *Lewis et al.*, 1997, 1999], although some mixing of trajectory-derived air masses in any given wind sector was probably inevitable. The clearest correspondences were observed for the NE and W wind sectors in EASE 96 (comprising 100% UK anti-cyclonic and 73% Westerly air, respectively) and for the SW and W wind sectors in EASE 97 (comprising 63% and 75% Polar air, respectively).[†] The SE wind sector was dominated by anti-cyclonic air from the UK and/or northern Europe in both campaigns (66% for EASE 96; 72% for EASE 97). It is important to note again, however, that only the periods identified with a particular ULe air mass type were included in the calculations presented in Fig. 4.3.

Comparison with the Institute of Terrestrial Ecology air mass classifications[‡]

Cape et al. [2000] analysed air masses arriving at Mace Head over the 3-year period 1995-1997 on the basis of the ECMWF 5-day back trajectories described in the last section, except that the arrival pressure level was chosen to be 900 mb, and only trajectory locations every 12 hours (rather than every 30 minutes) were used, so that the data set consisted of 10 time points for each trajectory. The average-linking cluster method was used to group the 30-dimensional (latitude, longitude and pressure, all at 10 time steps) data set, in a procedure designed to minimise within-cluster variance and maximise between-cluster variance. Five distinct trajectory clusters were identified, which could be described as follows: 1, long-range westerly/north-westerly flow over the North Atlantic; 2, easterly flow from the UK and originating in northern Europe; 3, south-westerly low-speed flow originating in the mid-Atlantic; 4, westerly/south-westerly high-speed flow, originating in the USA or Canada; and 5, northerly maritime flow, including trajectories over Scandinavia and northern Britain. Each 6 h period during EASE 96 and EASE 97 was allocated to a given trajectory cluster only if all four trajectories for that particular day belonged to the same cluster.

[†] It must be noted, however, that there were relatively few data in the NE sector in EASE 96 and the SW sector in EASE 97, as discussed further in Sections 4.3 and 4.5.

[‡] The trajectory cluster data were kindly provided by Dr J. Neil Cape, Institute of Terrestrial Ecology.

The comparison of the ITE trajectory clusters with the ULi wind sector classification was carried out by counting the number of minutes in each 6 h period belonging to each wind sector. Periods not allocated to any trajectory cluster by the ITE method were ignored. As in the last section, a two-way comparison was performed (Figures 4.4 and 4.5).

Fig. 4.4 (a) shows that for EASE 96, trajectory clusters 1,3 and 4 (all described by long-range flow over the Atlantic) largely comprised the three ‘westerly’ wind sectors, NW, SW and W (84, 100 and 68%, respectively). In contrast, clusters 2 and 5 were dominated by the SE wind sector (80 and 62%), with smaller contributions from other sectors. The pattern was very different in EASE 97 (Fig. 4.4 (b)), where the SE wind sector was the major contributor to all the trajectory clusters except 5 (northerly maritime flow), in which the contribution from the NW and NE sectors together was 50%. Even in this cluster, however, the SE wind sector contribution was significant (22%).

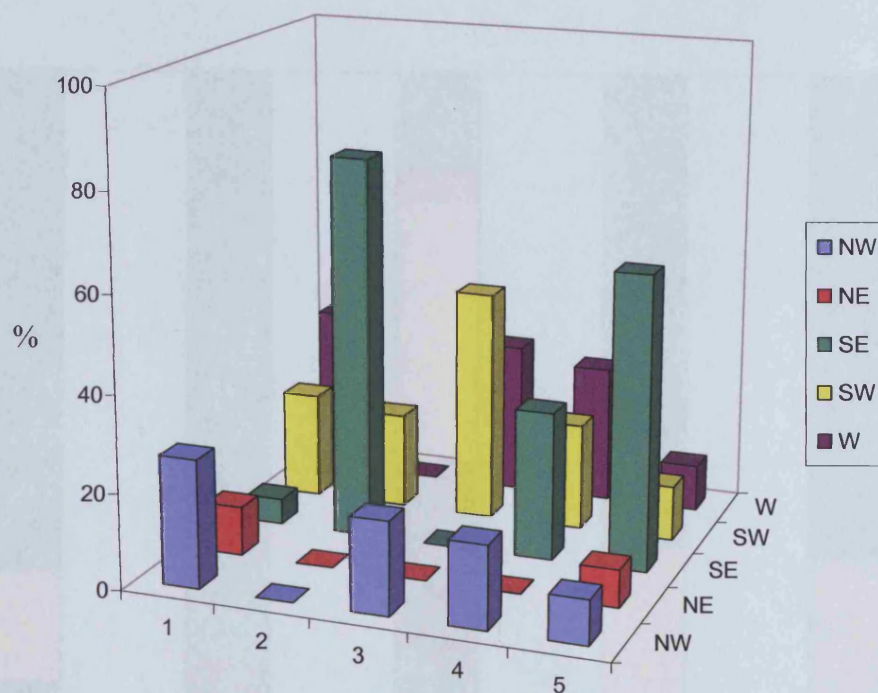
Fig. 4.5 shows the reverse comparison, where the fractional contribution of the trajectory clusters of *Cape et al.* [2000] to each ULi wind sector are indicated. During EASE 96, the composition of each of the three ‘westerly’ sectors, NW, SW and W, was very similar, dominated by clusters 1,3 and 4, and particularly 1 (70, 59 and 66%, respectively). The NE sector also comprised mainly cluster 1 (90%), whereas the composition of the SE wind sector was more mixed, with large contributions from clusters 4 (westerly/south-westerly high-speed flow from North America) and 5 (northerly maritime flow). In contrast, the contribution of the westerly flows (clusters 1,3 and 4) was much reduced in EASE 97, and northerly maritime flow (including trajectories over Scandinavia and northern Britain) represented a significant part of all five wind sectors, particularly NW, NE and W (61, 68 and 72%, respectively). Anti-cyclonic flow from the UK and northern Europe was most significant in the NW (30%) and SE (29%) sectors.

Summary of the air mass classification comparisons

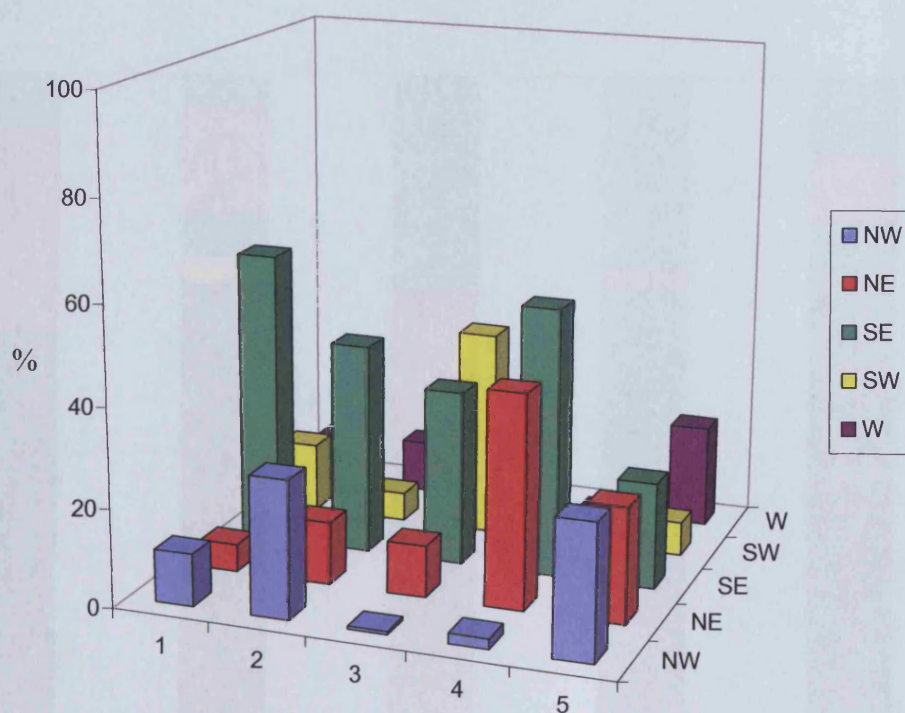
The two foregoing comparisons have shown, first and foremost, the striking differences in the meteorological conditions between the summer of 1996 (EASE 96) and the spring of 1997 (EASE 97) at Mace Head. In the summer campaign, westerly air flow over the Atlantic, whether from the mid-Atlantic at low latitudes or originating in North America, was very significant, whereas in EASE 97 the most important air mass type was clearly polar in origin. However, in a study of the ozone and carbon monoxide record at Mace Head in the period 1990-1994, *Derwent et al.* [1998] concluded that the ‘USA-Canada’ and ‘Greenland-Iceland’

Figure 4.4 Institute of Terrestrial Ecology wind trajectory clusters^a in terms of wind direction measured at Mace Head

(a) EASE 96



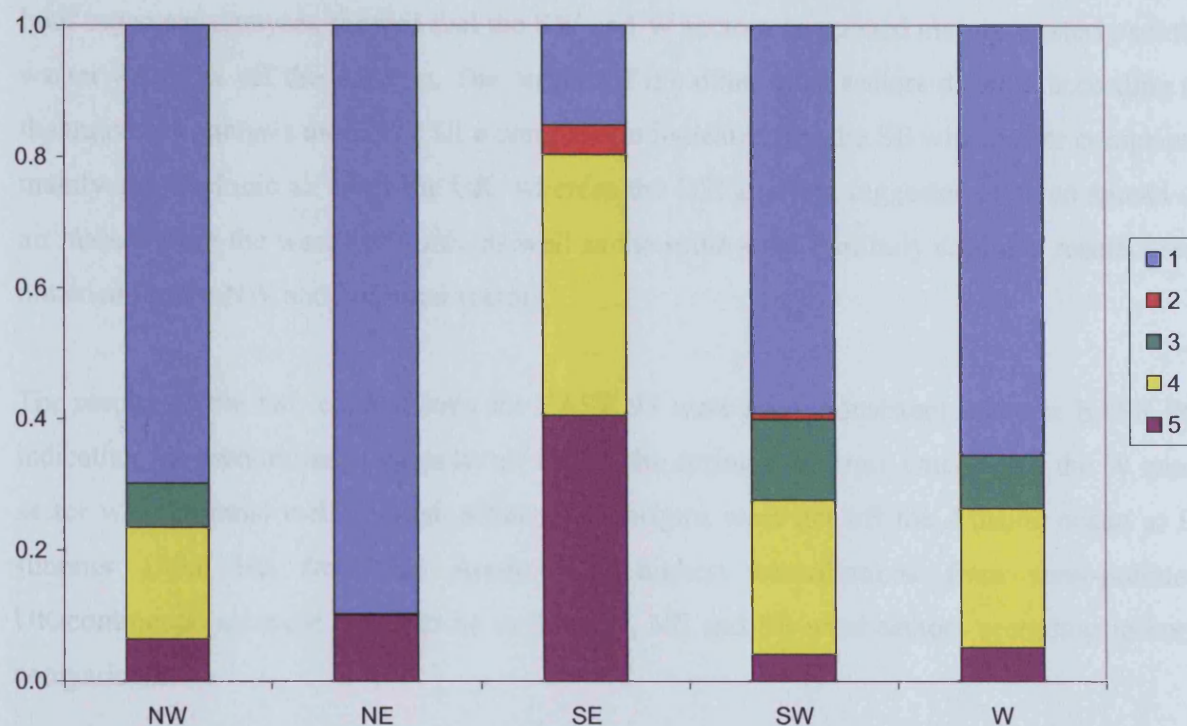
(b) EASE 97



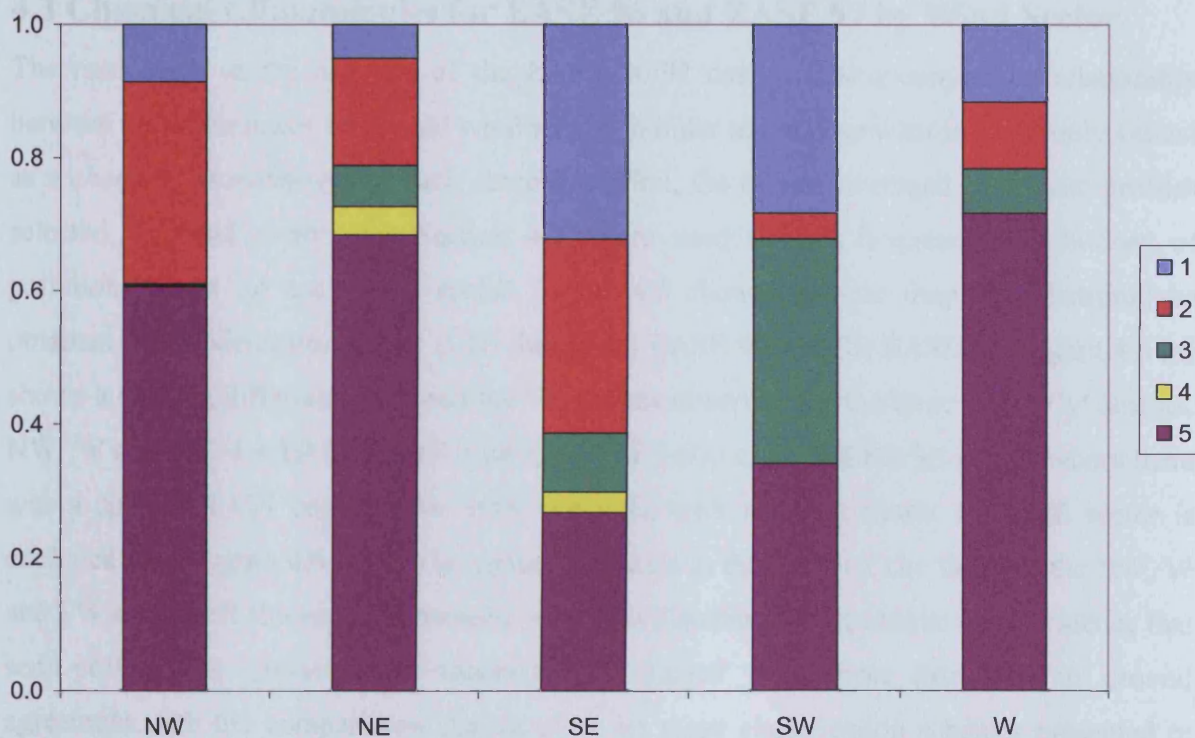
^aThe trajectory clusters are numbered 1-5 [Cape *et al.*, 2000]; see text for details.

Figure 4.5 Fractional contributions of Institute of Terrestrial Ecology trajectory clusters to each University of Leicester wind sector

(a) EASE 96



(b) EASE 97



air masses, in which ozone and carbon monoxide mixing ratios were generally very similar, comprised a common source region (see also Section 4.5.2).

In terms of the wind sectors used in the analyses in this thesis, clear differences in air mass origin were captured for EASE 96, particularly in the SW and W wind sectors as defined here: both trajectory analyses showed that the SW and W sectors comprised mainly westerly/south-westerly airflow off the Atlantic. The origins of the other three sectors differed according to the trajectory analysis used. The ULe comparison indicated that the SE wind sector comprised mainly anti-cyclonic air from the UK, whereas the ITE analysis suggested an even spread of air masses from the west and north, as well as the south-east. Similarly complex results were obtained for the NW and NE wind sectors.

The results of the two comparisons for EASE 97 were more consistent than for EASE 96, indicating the predominance of polar air during the spring campaign. Once again the W wind sector was the most well-defined, although its origins were not off the Atlantic ocean as in summer 1996, but from the Arctic. The highest contributions from semi-polluted UK/continental air were found to be in the NW, NE and SE wind sectors according to both comparisons.

4.3 Chemical Climatologies for EASE 96 and EASE 97 by Wind Sector

The next stage in the analysis of the EASE 96/97 data was to examine the relationship between pollution tracer levels and wind sector, in order to build up what is commonly known as a *chemical climatology* for each campaign. First, the minute-averaged composite profiles selected by wind sector (see Section 4.2) were used to plot frequency distributions of pollution tracers for each wind sector. Figure 4.6 shows example frequency distributions obtained for condensation nuclei (CN) during (a) EASE 96 and (b) EASE 97. Figure 4.6 (a) shows a striking difference between the CN counts observed for the three ‘westerly’ sectors, NW, W and SW, for EASE 96, all with modes of $5\text{--}600\text{ cm}^{-3}$, and the SE sector, where there was a spread of CN counts from 1000 upwards, with no clear mode. (The NE sector is excluded from Figure 4.6 (a) due to a paucity of data in this sector.) The fact that the NW, W and SW sectors all showed well-defined, unimodal distributions represents good evidence that semi-polluted air masses were successfully excluded from these data sets, in general agreement with the comparisons against other air mass classification schemes presented in Section 4.2. Broadly similar results were obtained from the CN distributions in EASE 97 (Fig.

4.6 (b)). The CN counts in the SE sector were considerably higher in EASE 97 (minimum *ca* 2800 cm⁻³, mode at *ca* 4000 cm⁻³), whilst the NW and SW (not shown) distributions showed a more significant tail to higher CN counts (modes both *ca* 700 cm⁻³). The W distribution was very similar to that obtained in 96 (mode at *ca* 600 cm⁻³), whilst the NE distribution was similar to that obtained for the SE sector in EASE 96.

Figure 4.7 shows the frequency distributions of NO_x/NO_y by wind sector for (a) EASE 96 and (b) EASE 97, where [NO_x] is [NO+NO₂], and NO_y represents the sum of all oxidised nitrogen species, including NO, NO₂, nitric acid, PAN and organic nitrates. The NO_x/NO_y distributions for EASE 96 were all ill-defined (Fig. 4.7 (a)), generally with no clear mode; this was probably owing to problems with the NO_y detection efficiency of the CRANOX instrument in the first EASE campaign, since [NO_x] was often calculated to exceed [NO_y], which is clearly not possible; higher quality data were obtained during the second campaign, in spring 1997. Fig. 4.7 (b) shows that the best-defined NO_x/NO_y distribution obtained in EASE 97 was for the W sector, with a single mode at 0.45, indicative of relatively aged air masses, not recently polluted. The NW distribution was more complex, although the main mode remained relatively low, at only 0.55. The NE sector showed an increased level of complexity, suggesting that relatively clean air masses from the Arctic were mixed with semi-polluted air from the UK and the continent in this case (*cf.* Figs 4.3 (b) and 4.5 (b)). The SE sector had the highest mode (0.65), as expected for more recently polluted air masses. The SW distribution contained relatively few NO_y data, and is not shown in Fig. 4.7 (b).

Table 4.3 summarises these results; also included are mean daytime (06:00-19:00 GMT) values for other selected tracers and temperature for both campaigns by wind sector. Table 4.3 shows that levels of pollution tracers such as NO_x, CO and CH₄ were significantly higher over all wind sectors in spring 1997 than in summer 1996. As mentioned in Section 4.1, winter maxima and summer minima in pollution tracers have been observed previously in the Northern Hemisphere [*e.g.*, Penkett and Brice, 1986; Honrath and Jaffe, 1992; Derwent *et al.*, 1998], and ascribed to varying levels of photochemical activity through the seasons. It is also worth noting that the average ozone levels were fairly uniform across the wind sectors, with the exception of the SW and W sectors in EASE 96, which exhibited slightly lower ozone mixing ratios than any other sector in either campaign. This difference is probably indicative of long-range transport of relatively clean air to Mace Head in summer 1996, from oceanic regions where net ozone destruction is likely (see Section 4.5). Such air masses were far less frequently encountered in EASE 97 (Section 4.2), relative to semi-polluted air masses from

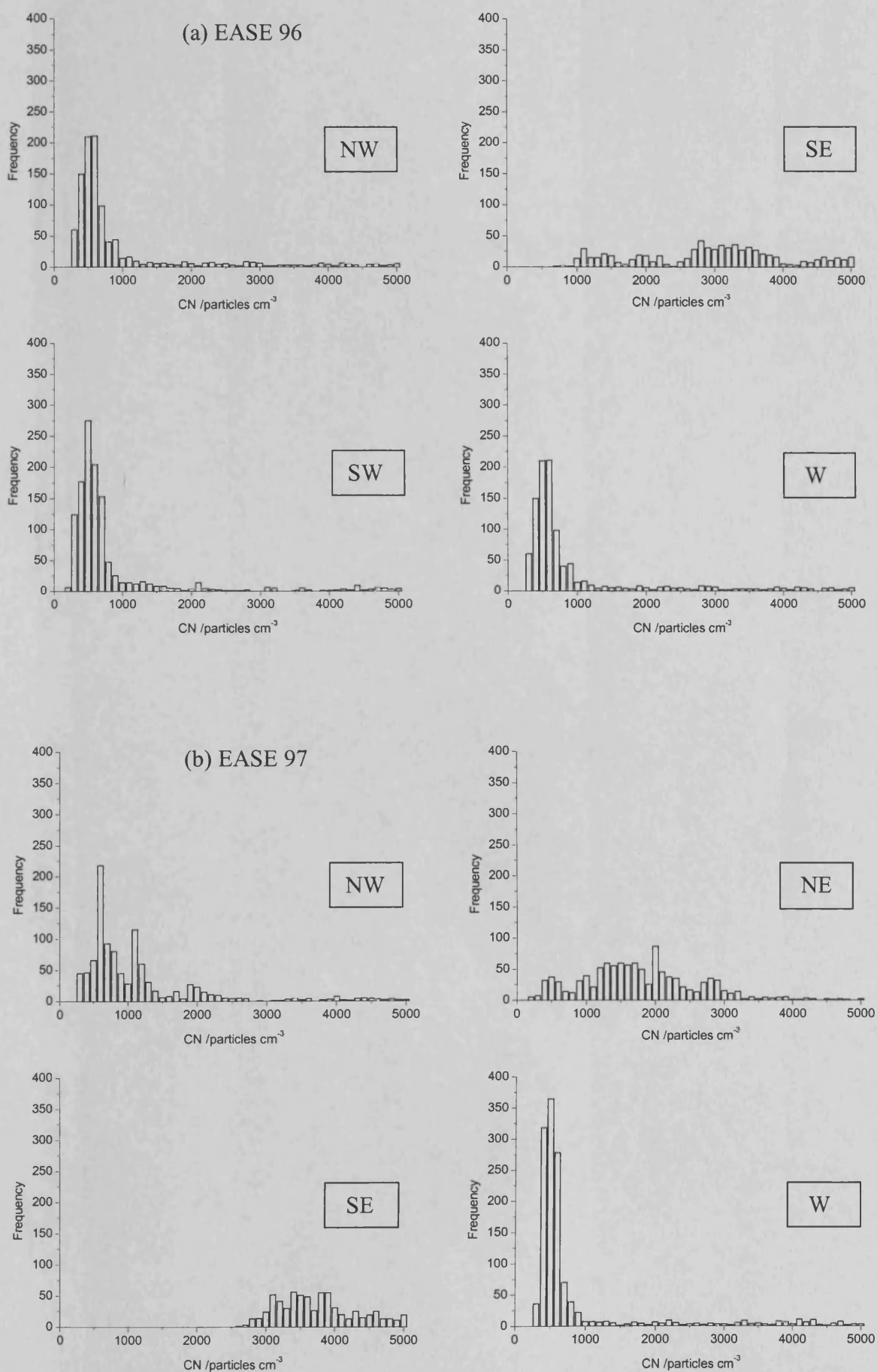
Figure 4.6 CN frequency distributions (minute averaged data) during the EASE campaigns

Figure 4.7 NO_x/NO_y frequency distributions (minute averaged data) during the EASE campaigns (note change of scale on y-axis in panel (b))

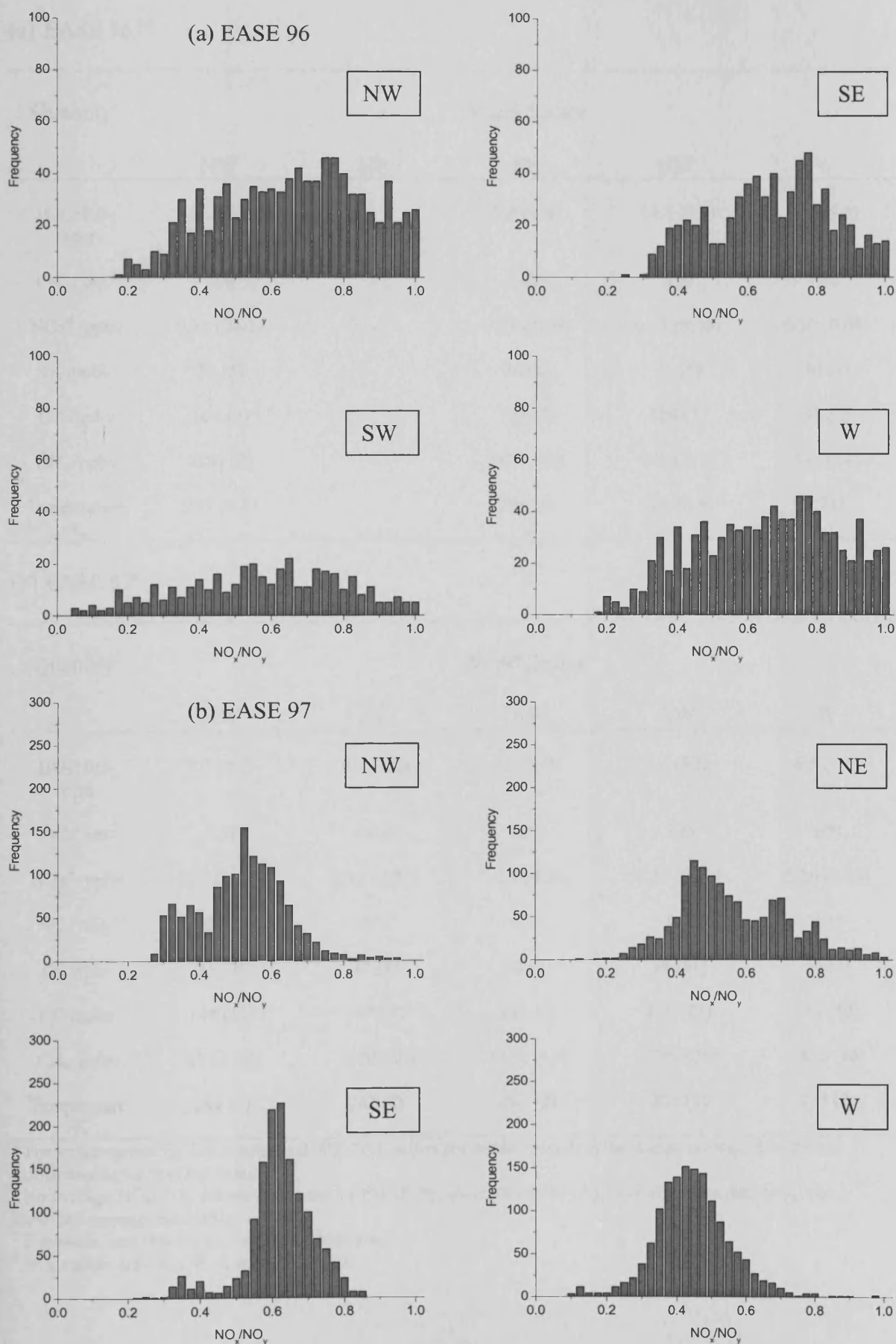


Table 4.3 Modes and daytime averages (06:00-19:00 GMT) of selected tracers and temperature during (a) EASE 96 and (b) EASE 97

(a) EASE 96^{a,b}

Quantity ^c	Wind Sector				
	NW	NE	SE	SW	W
HO ₂ +RO ₂ /pptv	13.2 (5.0)	-	9.4 (4.6)	11.8 (3.9)	9.9 (5.1)
CN ^a / cm ⁻³	600	-	2800	500	600
NO _x ^d /ppbv	0.12 (0.05)	-	0.91 (0.40)	0.15 (0.10)	0.10 (0.04)
O ₃ /ppbv	37 (5)	-	36 (6)	27 (5)	30 (3)
CO /ppbv	104 (2)	-	128 (8)	104 (7)	98 (3)
CH ₄ /ppbv	1789 (2)	-	1828 (22)	1783 (10)	1783 (4)
Temperature /K	287 (0.5)	-	289 (1)	289 (0.5)	287 (1)

(b) EASE 97^a

Quantity ^c	Wind Sector				
	NW	NE	SE	SW	W
HO ₂ +RO ₂ /pptv	9.7 (4.7)	6.5 (3.2)	9.3 (3.0)	7.7 (5.6)	6.6 (3.5)
CN ^a / cm ⁻³	700	1800	4000	700	600
NO _x ^d /ppbv	0.31 (0.11)	0.31 (0.27)	1.29 (0.34)	0.28 (0.10)	0.26 (0.20)
NO _x /NO _y ^a	0.55	0.5	0.65	0.2	0.45
O ₃ /ppbv	35 (2)	37 (4)	38 (2)	34 (11)	34 (2)
CO /ppbv	144 (11)	148 (9)	165 (6)	130 (23)	151 (13)
CH ₄ /ppbv	1822 (9)	1820 (20)	1852 (13)	1799 (25)	1826 (16)
Temperature /K	284 (1)	282 (2)	287 (2)	286 (2)	283 (2)

^a The values given for CN counts and NO_x/NO_y ratios are modes based on the minute-averaged frequency distributions (see text for details).

^b No average NO_x/NO_y values are given for EASE 96, since measured NO_y was often less than NO_x, and therefore deemed unreliable.

^c Figures in brackets are 1σ standard deviations.

^d NO_x values are CRANOX measurements.

Europe; this feature of the climatology at Mace Head has been reported previously by Derwent *et al.* [1998].

4.4 The PERCA Measurements during EASE 96 and EASE 97

4.4.1 Introduction

Before continuing in the analysis of the EASE 96/97 data by wind sector, it is worthwhile to consider the general performance of the UEA-Leicester PERCA instrument during the two campaigns. To this end, a comparison of the peroxy radical mixing ratios observed in summer 1996 and spring 1997 is presented in the next section. It is assumed in the analyses presented in this chapter that any PERCA measurement deficit owing to ambient humidity was equal for both the summer campaign in 1996 and the spring campaign in 1997. This is something of a simplification, but it will be shown in Chapter 6 that the expected mean underestimation factors were 1.8 for EASE 96 and 1.6 for EASE 97. These figures are only *ca* 12% different, which is considerably less than the total estimated instrumental uncertainty ($\pm 35\%$, see Chapter 2) and is therefore not considered further here. However, the likely systematic underestimation of peroxy radical mixing ratios by the PERCA technique during the EASE campaigns is considered fully in Sections 4.5 and 4.6.

4.4.2 Comparison of peroxy radical mixing ratios during EASE 96 and EASE 97

The data coverage of the PERCA instrument during both EASE campaigns was excellent: 97% and 95%, respectively (based on hourly data). Once the minimum wind speed of 3 m s^{-1} criterion was applied to the minute-averaged data, 80% remained for analysis for EASE 96, and 68% for EASE 97. Once the wind speed and wind direction criteria were applied to the hourly averaged data, 84% of hours remained for EASE 96 and 80% for EASE 97. The PERCA data coverage in this selected hourly data set was 97% for EASE 96 and 94% for EASE 97.

The full time series of measurements (10 min averages) are plotted in Figures 4.8 (EASE 96) and 4.9 (EASE 97). Measurements of $j(\text{O}^1\text{D})$ (the photolysis frequency for the process $\text{O}_3 \rightarrow \text{O}^1\text{D})$ are plotted on a secondary axis, for comparison. Qualitatively, it is clear from Figs 4.8 and 4.9 that peroxy radical levels were generally higher in summer (96) than in spring (97); in fact, the daytime average $[\text{HO}_2 + \text{RO}_2]$ was 12.1 pptv in EASE 96, compared with only 8.5 pptv in EASE 97. Since peroxy radicals are reactive species, with daytime lifetimes of the

order of a few minutes (*cf.* Chapter 3), it can be assumed first, that *in-situ* chemical production and loss processes control their concentrations, with no need to consider transport to or from a given site, and second, that peroxy radical concentrations react sufficiently rapidly to perturbations in the production/loss reaction rates that the steady-state approximation may be used in their calculation. Penkett *et al.* [1997] used such an approximation to show that, in relatively clean air, where $[\text{NO}_x]$ is low, the sum of peroxy radicals, $[\text{HO}_2 + \text{RO}_2]$, may be approximated by:

$$[\text{HO}_2 + \text{RO}_2] = \left(\frac{f \cdot j(\text{O}^1\text{D}) \cdot [\text{O}_3]}{k'} \right)^{1/2} \quad (4.1)$$

where f is the fraction of singlet oxygen atoms that react with water, rather than undergo collisional deactivation to ground-state oxygen atoms ($\text{O}(^3\text{P})$), and CH_3O_2 is considered to be the dominant organic peroxy radical present.

Figure 4.8 PERCA measurement time series (10 min averages) for EASE 96

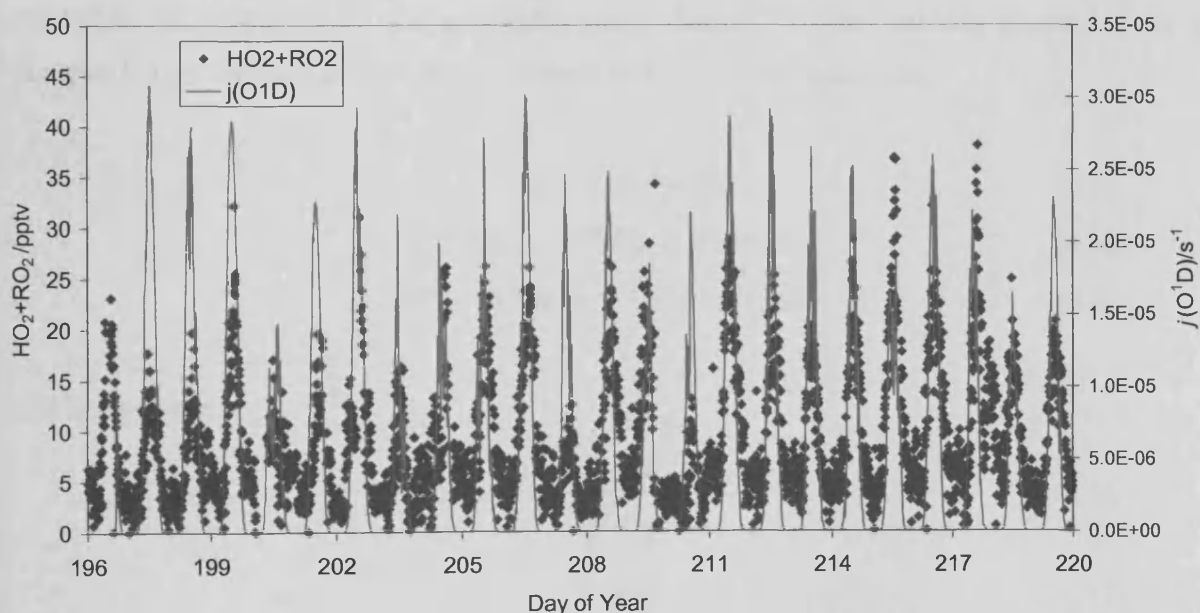
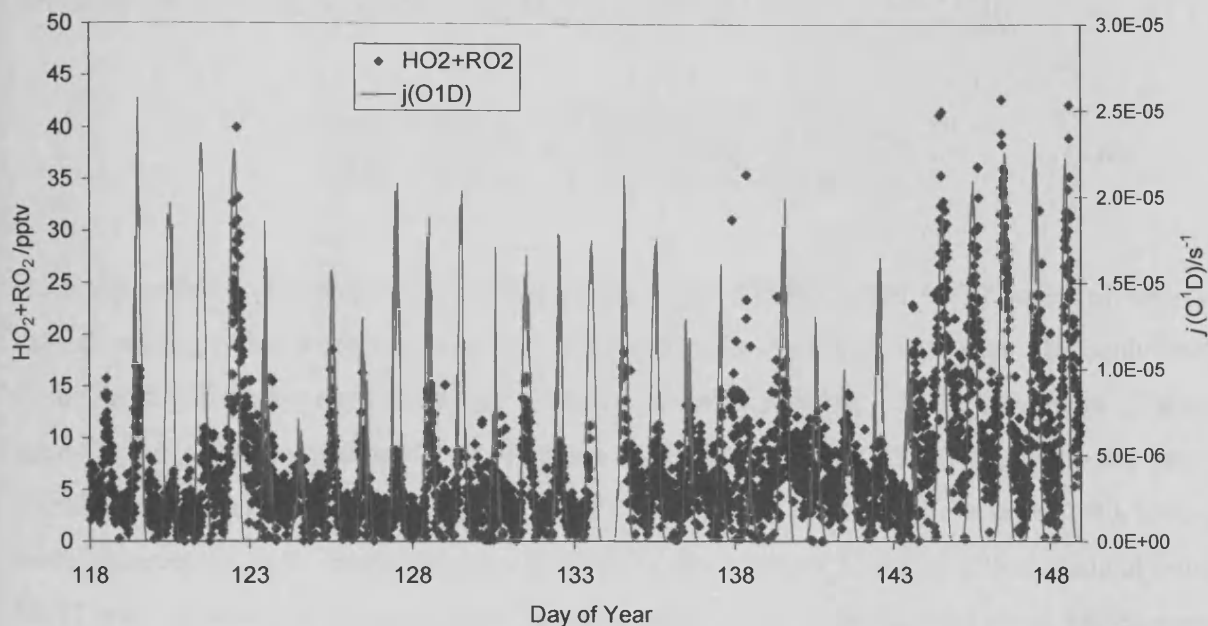


Figure 4.9 PERCA measurement time series (10 min averages) for EASE 97^a

^aThe discontinuity in the peroxy radical measurements on Day 143 (23rd May 1997) was caused by a change of luminol solution, and consequent change in sensitivity of the Scintrex NO₂ detector (see Chapter 2). This effect is difficult to remove from the data, and has therefore not been considered further in the analyses presented in the following sections.

Equation (4.1) also neglects peroxy radical sources other than ozone photolysis, such as photolysis of formaldehyde or peroxides (see Chapter 5). The quantity denoted k' is a composite rate constant for the peroxy radical self- and cross- reactions,



and is given by:

$$k' = \frac{\beta^2 k_2 + \beta k_4 + k_3}{(\beta + 1)^2} \quad (4.5)$$

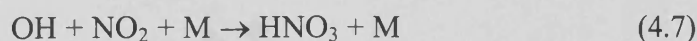
where k_i is the rate coefficient for the reaction (4.i) and $[\text{HO}_2] = \beta[\text{CH}_3\text{O}_2]$ [Monks *et al.*, 1998]. Calculations showed that the only factor in f to change significantly between EASE 96 and EASE 97 was the vapour pressure of water. Furthermore, k' was found to change very little between the two campaigns (mean 96/97 ratio 1.03), irrespective of the HO₂/RO₂ ratio (assuming this ratio to be constant between seasons; see later, and also Chapter 5). Hence,

under relatively unpolluted conditions, the ratio of peroxy radicals measured in EASE 96 versus EASE 97 could be approximated by

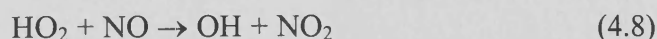
$$\frac{[\text{HO}_2 + \text{RO}_2]_{96}}{[\text{HO}_2 + \text{RO}_2]_{97}} = \sqrt{\frac{j(\text{O}^1\text{D})_{96} \cdot [\text{O}_3]_{96} \cdot [\text{H}_2\text{O}]_{96}}{j(\text{O}^1\text{D})_{97} \cdot [\text{O}_3]_{97} \cdot [\text{H}_2\text{O}]_{97}}} \quad (4.6)$$

Both the midday (12:00-13:00) and daytime-average (06:00-19:00) 96/97 ratios of peroxy radical mixing ratios were found to be 1.4 over the whole of both data sets. The equivalent ratios for the products (right-hand side of Equation 4.6) were both 1.3. The agreement of these ratios is very good, considering the limitations of the approach. However, when the same calculations were carried out using only the W wind sector data, where the lowest NO_x levels were observed in each campaign (see Table 4.3), the measured midday peroxy radical ratio 96/97 was 1.6, whereas the equivalent 'product' ratio was 1.1; the daytime mean values were 2.1 and 1.4, respectively.

It is not immediately clear why this simple treatment of the data should work better over the whole campaign data set than for the relatively clean W wind sector only, given that relatively polluted (SE) air masses would necessarily be included in the former calculation. There are two main assumptions inherent in Equation (4.1). The first is that the dominant peroxy radical loss processes are the self- and cross-reactions (reactions 4.2-4.4), and that the $\text{OH} + \text{NO}_2$ reaction (4.7) is of minor importance [Penkett *et al.*, 1997].



However, as noted in Section 4.1, NO_x levels were considerably higher in 97 than in 96, which would tend to suppress peroxy radical levels in 97 relative to 96, owing to the faster recycling of HO_2 to OH :



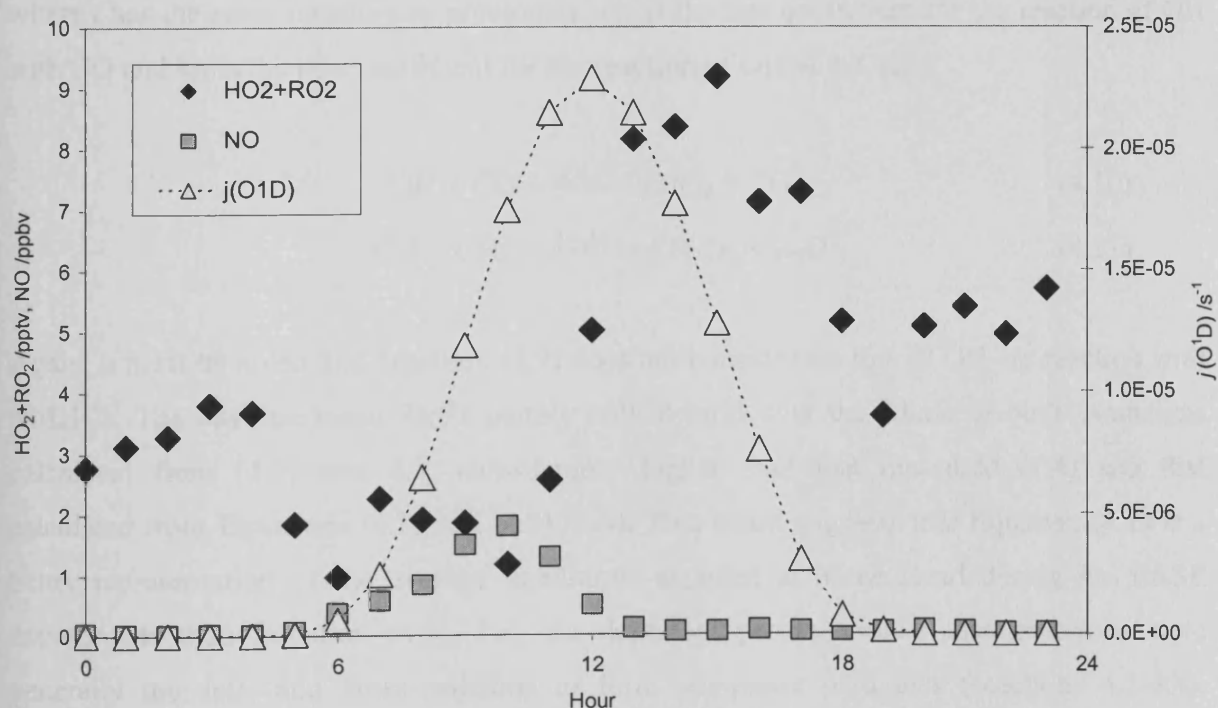
A good example of this process was observed on 1st May during EASE 97 (Figure 4.10), when NO levels in the morning reached 2 ppbv, and the sum of peroxy radicals was suppressed to <3 pptv. Between 11:00-13:00 GMT, NO mixing ratios subsided to <100 pptv, and the peroxy radical levels recovered to typical midday mixing ratios of 8-10 pptv. The

smooth, symmetric $j(\text{O}^1\text{D})$ trace for that day (also shown in Fig. 4.10) shows that there were no important cloud effects on 1st May to complicate this interpretation of the data.

The 96/97 mean daytime NO_x ratio was 0.54 for all campaign data, but considerably lower (0.38) for the W wind sector only; this difference would tend to increase suppression of peroxy radical mixing ratios in EASE 97 relative to EASE 96 more in the W wind sector than in the campaign data set as a whole.

The second assumption in Equation (4.1) is that NMHCs do not contribute significantly to the peroxy radical population [Penkett *et al.*, 1997]. This assumption can be justified for Mace Head by consideration of the OH loss (*i.e.* peroxy radical formation) data presented by Carslaw *et al.* [1999a] for EASE 96, where an average of 80% of OH loss was calculated to be due to reaction with CO and CH_4 ; and by Carslaw *et al.* [2001a] for EASE 97, where at least 80% of OH loss was calculated to be *via* reaction with CO and CH_4 throughout the campaign. The average percentage OH loss attributable to these species during EASE 97 was *ca* 90%, reaching 95% on clean days.

Figure 4.10 Peroxy radical, NO and $j(\text{O}^1\text{D})$ time series for 1st May 1997 (EASE 97 campaign)

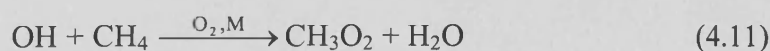


However, a further complication inherent in Equation (4.6) is that the $\text{HO}_2/\text{CH}_3\text{O}_2$ ratio is unlikely to have been the same for both campaigns, given the change in CO/CH_4 ratio from EASE 96 to EASE 97 (see data in Table 4.3). Considering first the campaigns as a whole, the mean daytime CO/CH_4 ratio changed from 0.06 to 0.09 between summer 1996 and spring 1997, giving a 96/97 ratio for this quantity of 0.72. For the W data only, the CO/CH_4 ratio changed from 0.05 to 0.08, giving a 96/97 ratio of 0.66. This observation means that the $\text{HO}_2/\text{CH}_3\text{O}_2$ ratio (and hence k') is likely to have increased more in the W data subset than in the campaign-averaged conditions. This effect alone might explain the discrepancy between the measured 96/97 $[\text{HO}_2 + \text{RO}_2]$ ratio and the 'product' ratio (right-hand side of Equation 4.6) in the W wind sector, but would also imply that the good agreement obtained for the campaign-averaged data was to some extent fortuitous.

The applicability of Equation (4.1) was further tested by calculating the daytime 96/97 peroxy radical ratio assuming that the peroxy radical losses were dominated by recycling to OH (reaction 4.8), followed by OH reaction with NO_2 to give HNO_3 (reaction 4.7). This approach yields Equation (4.9), after Penkett *et al.* [1997]:

$$[\text{HO}_2 + \text{RO}_2] = \frac{2f \cdot j(\text{O}^1\text{D})[\text{O}_3]}{k_7[\text{NO}_2]} \left(\frac{k_{10}[\text{CO}] + k_{11}[\text{CH}_4]}{k_8[\text{NO}]} \right) \quad (4.9)$$

where f has the same meaning as previously, k_{10} is the rate coefficient for the reaction of OH with CO and k_{11} is the rate coefficient for the reaction of OH with CH_4 :



Again, it must be noted that Equation (4.9) does not consider the loss of OH *via* reaction with NMHCs. The daytime mean 96/97 peroxy radical ratio over the whole of both campaigns calculated from (4.9) was 4.5, considerably higher than that measured (1.4) and that calculated from Equations (4.1) and (4.5) (1.3). This result suggests that Equation (4.1) is a better representation of the average conditions sampled at Mace Head during the EASE experiments than Equation (4.9), *i.e.*, the dominant peroxy radical loss processes were generally the self- and cross-reactions to form gas-phase peroxides (reactions 4.2-4.4). However, clearly Equations (4.1) and (4.9) represent two extreme situations: Equation (4.1)

represents the hypothetical case where $[\text{NO}_x]$ is zero and hence the loss of peroxy radicals is entirely through their self- and cross-reactions (see also Chapter 5); Equation (4.9) represents the case where $[\text{NO}_x]$ is sufficiently high that the peroxy radical self- and cross-reactions may be neglected entirely. Neither of these extremes generally applies without reservations to the real atmosphere [*cf. Zanis et al.*, 1999].

4.5 Photochemical Ozone Tendencies during the EASE Campaigns

4.5.1 Day-by-day analysis

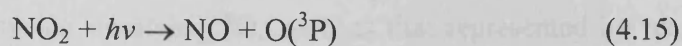
As discussed in Section 4.1.1, a broad ozone maximum in the spring and a minimum in the summer have been reported from a number of different locations in both the boundary layer and the free troposphere in the Northern Hemisphere [*e.g.*, *Derwent et al.*, 1998; *Monks*, 2000, and references therein]. In order to assess the role of photochemistry in this annual cycle, it is useful to investigate the seasonal ozone budget at remote sites such as Mace Head, where both relatively clean air masses advected from the Arctic and mid-Atlantic, and polluted air masses originating in the UK and continental Europe, are regularly encountered [*e.g.*, *Simmonds et al.*, 1997]. The *ozone tendency*, or net photochemical production rate of ozone ($N(\text{O}_3)$), is a useful measure of the ozone productivity of an air mass, which neglects entrainment from aloft and deposition processes (*cf.* Chapter 5, Equation 5.4). Ozone tendencies were calculated in this work by two different methods. The first method was based on use of the measured peroxy radicals to calculate the ozone production term, and may be expressed as

$$N(\text{O}_3) = k_P[\text{NO}][\text{HO}_2 + \text{RO}_2] - \{fj(\text{O}^1\text{D}) + k_{13}[\text{OH}] + k_{14}[\text{HO}_2]\}[\text{O}_3] \quad (4.12)$$

where k_P is a combined rate coefficient for the oxidation of NO to NO_2 by all peroxy radicals, and k_{13} and k_{14} are the rate coefficients for reactions (4.13) and (4.14), respectively.



The first term in Equation (4.12) represents the only known ozone production route in the troposphere (see also Chapter 1), namely the oxidation of NO to NO_2 , followed by photolysis of NO_2 to give ground-state oxygen atoms, $\text{O}(^3\text{P})$, which then combine with oxygen to give ozone:



$$(\lambda < 420 \text{ nm})$$



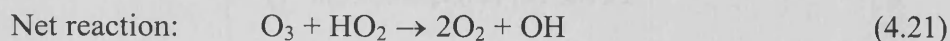
The other terms in Equation (4.12) represent the major ozone loss processes occurring in the troposphere. As HO_2 measurements were not available throughout both campaigns, $\text{N}(\text{O}_3)$ was calculated from Equation (4.12) in three scenarios, with HO_2 comprising 0.25, 0.50 and 0.75 of the total peroxy radical population ($\text{HO}_2 + \text{RO}_2$). Similarly, $[\text{OH}]$ was estimated from the low- NO_x steady-state expression derived by Penkett *et al.* [1997]:

$$[\text{OH}] = \frac{2f \cdot j(\text{O}^1\text{D})[\text{O}_3]}{k_{10}[\text{CO}] + k_{11}[\text{CH}_4]} \quad (4.17)$$

Equation (4.17) once again neglects sources of OH other than ozone photolysis, as well as loss of OH *via* reaction with NMHCs, as discussed in Section 4.4.2. This approximate treatment could be justified by the fact that the low- NO_x expression for $[\text{HO}_2 + \text{RO}_2]$ (Equation 4.1), based on the same assumptions, gave a campaign-averaged 96/97 peroxy radical ratio in reasonable agreement with the measurements (but see caveats to this argument in Section 4.4.2). In addition, the contribution of the $\text{OH} + \text{O}_3$ reaction to overall ozone loss is generally relatively small (all-campaign daytime mean values using Equation (4.17) <10% for both EASE 96 and EASE 97), so that, for example, a 50% error in OH would only propagate as <5% in the $\text{N}(\text{O}_3)$ calculation.

In order to take account of the likely systematic underestimation of $[\text{HO}_2 + \text{RO}_2]$ by the PERCA technique in the marine boundary layer, where humidity is high, $\text{N}(\text{O}_3)$ values for EASE 96 and 97 were calculated both using the peroxy radicals as measured and using the measured values multiplied by two (see Section 4.4.1 and Chapter 6). In effect, these calculations represent lower and upper limits for $\text{N}(\text{O}_3)$, although possible loss of ozone *via* reaction with radicals other than HO_2 and OH are neglected in this analysis [*cf. Monks et al.*, 2000]. Recent work [Alicke *et al.* 1999; Carpenter *et al.*, 1999; Allan *et al.*, 2000a] has indicated the presence of photochemically produced halogen oxides, in particular iodine monoxide (IO), in the marine boundary layer at mid-latitudes. McFiggans *et al.* [1999] have shown from measurements at Mace Head during EASE 97 and at Tenerife during the Hillcloud component of the Aerosol Characterisation Experiment 2 (ACE 2), as well as

modelling studies, that catalytic cycles involving IO, such as that represented by reactions (4.18-4.21), have the potential to destroy ozone.



The model results of *Dickerson et al.* [1999] suggest that analogous bromine chemistry could also have an impact on the ozone budget in parts of the remote marine boundary layer, although the only direct measurements of bromine monoxide (BrO) at mid-latitudes thus far were made in the rather unusual environment of the Dead Sea basin [*Hebestreit et al.*, 1999].

The second method of estimating $\text{N}(\text{O}_3)$ utilised the photostationary state (PSS) expression (see Chapter 1), assuming that only ozone and peroxy radicals oxidise NO to NO_2 [*e.g.*, *Volz-Thomas et al.*, 1997]:

$$j(\text{NO}_2)[\text{NO}_2] = \{k_{23}[\text{O}_3] + k_p[\text{HO}_2 + \text{RO}_2]\}[\text{NO}] \quad (4.22)$$

where k_{23} is the rate coefficient for the reaction of ozone with NO:



Since, from Equation (4.12) the rate of production of ozone, $\text{P}(\text{O}_3)$, = $k_p[\text{NO}][\text{HO}_2 + \text{RO}_2]$, Equation (4.22) rearranges to give

$$\text{P}(\text{O}_3) = j(\text{NO}_2)[\text{NO}_2] - k_{23}[\text{NO}][\text{O}_3] \quad (4.24)$$

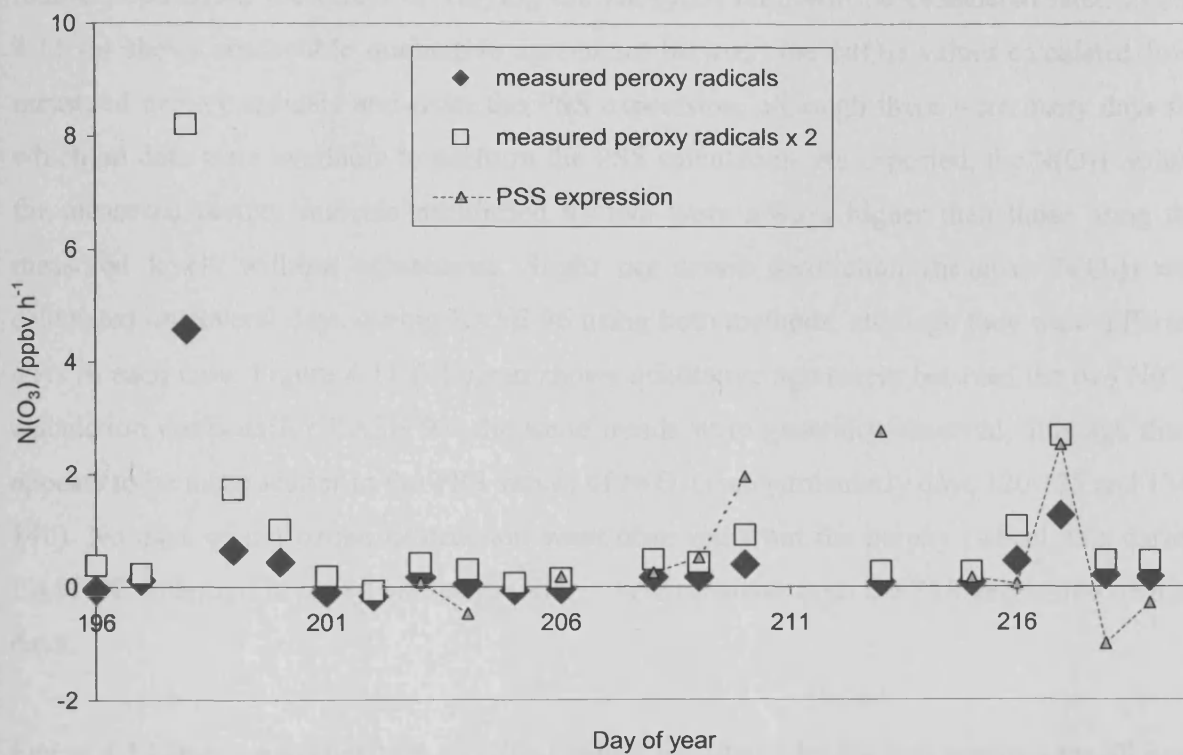
and hence:

$$\text{N}(\text{O}_3) = j(\text{NO}_2)[\text{NO}_2] - k_{23}[\text{NO}][\text{O}_3] - \{fj(\text{O}^1\text{D}) + k_{13}[\text{OH}] + k_{14}[\text{HO}_2]\}[\text{O}_3] \quad (4.25)$$

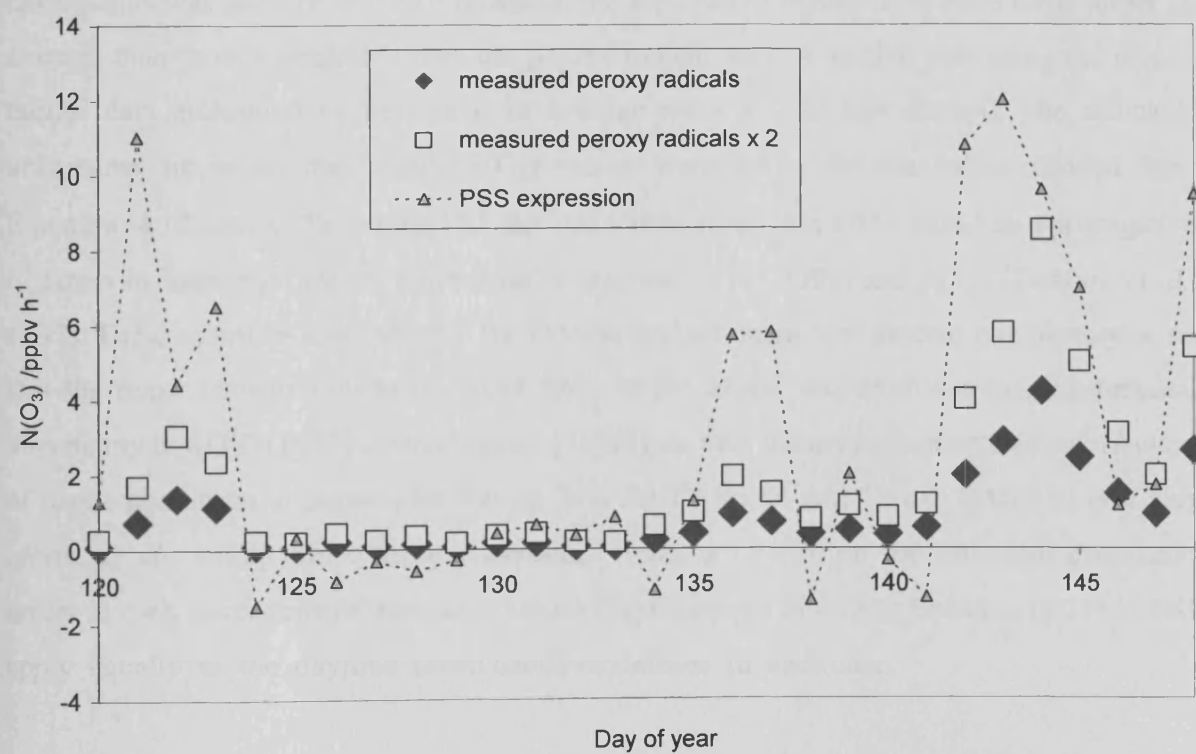
Figure 4.11 shows the ozone tendency time series calculated by the two distinct methods for (a) EASE 96 and (b) EASE 97. The CRANOX NO_x data were used throughout. Values for

Figure 4.11 Ozone tendencies during the EASE campaigns (06:00-19:00 GMT daytime means)

(a) EASE 96



(b) EASE 97



each day are averages over the daytime period, 06:00-19:00 GMT, in each case. $N(O_3)$ values calculated from Equation (4.12) using both the peroxy radicals as measured and the measured peroxy radicals multiplied by two are included for the purposes of comparison. All $N(O_3)$ values shown in Figures 4.11 (a) and (b) assume that HO_2 made up 50% of the total peroxy radical population; the effect of varying the HO_2/RO_2 ratio will be considered later. Figure 4.11 (a) shows reasonable qualitative agreement between the $N(O_3)$ values calculated from measured peroxy radicals and from the PSS expression, although there were many days for which no data were available to perform the PSS calculation. As expected, the $N(O_3)$ values for measured peroxy radicals multiplied by two were always higher than those using the measured levels without adjustment. Slight net ozone destruction (negative $N(O_3)$) was calculated on several days during EASE 96 using both methods, although they were different days in each case. Figure 4.11 (b) again shows qualitative agreement between the two $N(O_3)$ calculation methods for EASE 97: the same trends were generally observed, although there appears to be more scatter in the PSS values of $N(O_3)$ (see particularly days 120-125 and 134-140). No days of net ozone destruction were observed from the peroxy radical data during EASE 97, although negative values for $N(O_3)$ were obtained from the PSS expression on nine days.

Figure 4.12 shows a scatter plot of $N(O_3)$ values calculated by the two methods for all days from both campaigns where data were available. The level of correlation between the two calculations was good ($r^2 = 0.64$); however, the PSS $N(O_3)$ values were three times larger on average than those calculated from the peroxy radical data. A similar plot using the peroxy radical data multiplied by two gave an average ratio of 1.63 (not shown). The estimated uncertainty limits on the hourly $N(O_3)$ values were $\pm 46\%$ for the values derived from Equation (4.12) and $\pm 37\%$ on the PSS-derived values (Equation 4.25), based on a propagation of errors in individual measurements [*cf. Carpenter et al.*, 1998] and in k_{23} [*DeMore et al.*, 1997]. These estimates assumed that the most important ozone loss process was photolysis, so that the major contribution to the error limit in the ozone loss term was the experimental uncertainty in $j(O^1D)$ ($\pm 30\%$; *Monks et al.* [1998]). In fact, the average calculated contribution of ozone photolysis to ozone loss was *ca* 74% for EASE 96 and 71% in EASE 97 [see also *Monks et al.*, 2000]. Since these uncertainty limits are based on the estimated systematic errors in each measurement, the same values (Equation (4.12) $\pm 46\%$; Equation (4.25) $\pm 37\%$) apply equally to the daytime mean ozone tendencies in each case.

Figure 4.12 Scatter plot of daytime mean ozone tendency values calculated from peroxy radical data and from PSS perturbation (daytime mean values) for both EASE campaigns combined

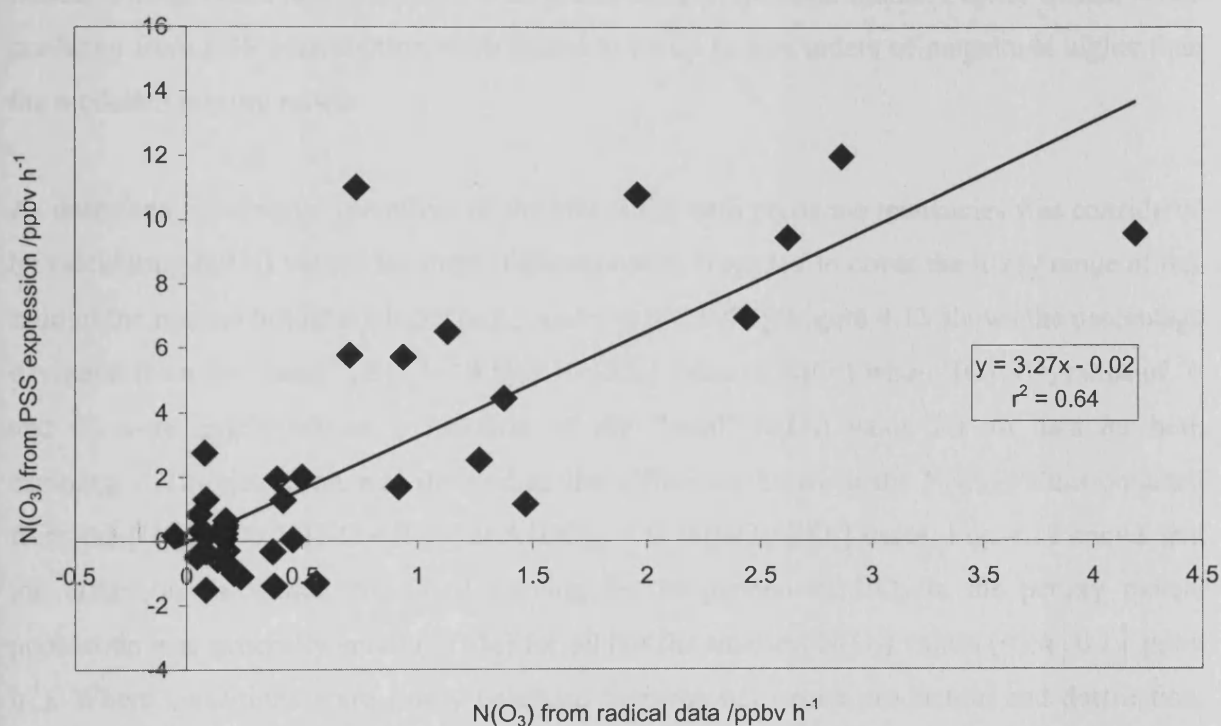
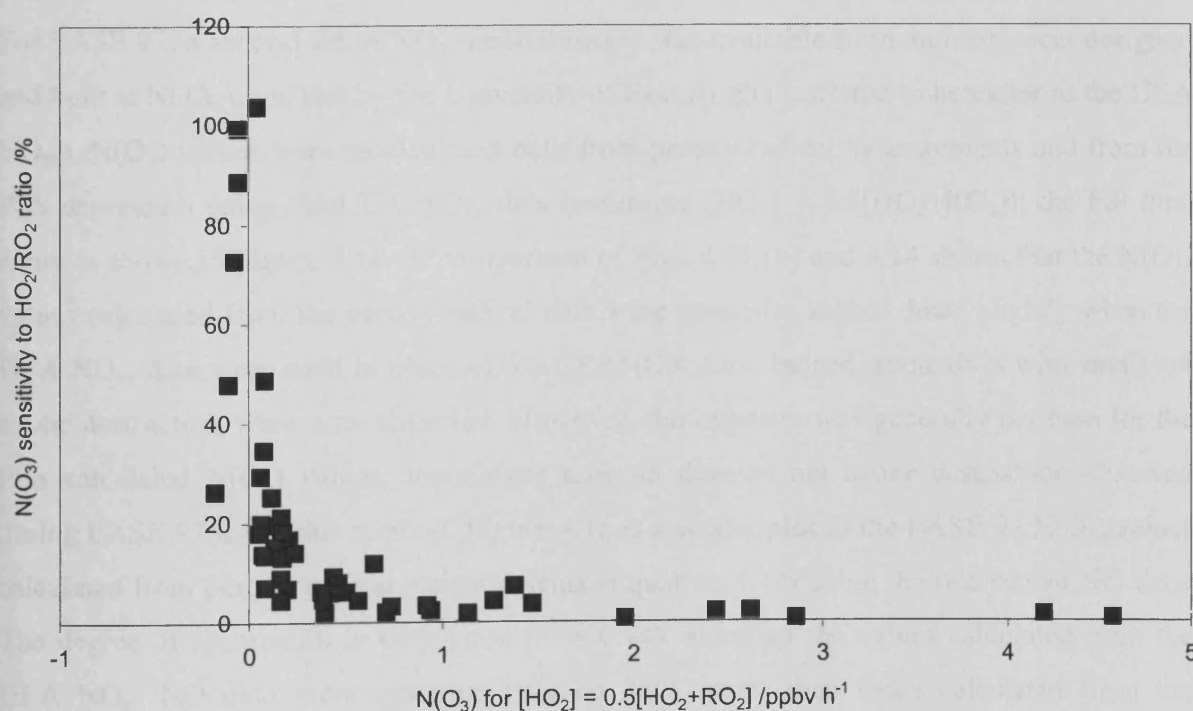


Figure 4.13 Sensitivity of peroxy radical derived ozone tendency values to HO_2/RO_2 ratio (see text for details) for both EASE campaigns combined



Clearly these limits are insufficient to explain the discrepancy shown in Fig. 4.12, even if the measured peroxy radicals were multiplied by two throughout the data set. A similar result was obtained by *Carpenter et al.* [1998], where PSS calculations were used to predict peroxy radical mixing ratios and compared with predictions from a box model. Peroxy radical levels predicted from PSS perturbation were found to be up to two orders of magnitude higher than the modelled mixing ratios.

As described previously, the effect of the HO_2/RO_2 ratio on ozone tendencies was considered by calculating $\text{N}(\text{O}_3)$ values for three different cases, intended to cover the likely range of this ratio in the marine boundary layer [e.g., *Ayers et al.*, 1997]. Figure 4.13 shows the percentage deviation from the 'basal' $[\text{HO}_2] = 0.5[\text{HO}_2 + \text{RO}_2]$ value of $\text{N}(\text{O}_3)$ when HO_2/RO_2 ratios of $1/3$ and $2/3$ were employed, as a function of the 'basal' $\text{N}(\text{O}_3)$ value for all data for both campaigns. The deviation was defined as the difference between the $\text{N}(\text{O}_3)$ values obtained from the $[\text{HO}_2] = 0.75[\text{HO}_2 + \text{RO}_2]$ and $[\text{HO}_2] = 0.25[\text{HO}_2 + \text{RO}_2]$ cases. Fig. 4.13 shows that the effect on calculated $\text{N}(\text{O}_3)$ of varying the proportion of HO_2 in the peroxy radical population was generally small ($< 20\%$) for all but the smallest $\text{N}(\text{O}_3)$ values ($< ca \mid 0.1 \mid \text{ppbv h}^{-1}$). Where conditions were finely balanced between net ozone production and destruction, the potential percentage error was very large (up to $\pm 100\%$). However, the absolute magnitude of the error from the HO_2/RO_2 ratio was estimated to be less than $ca \mid 0.1 \mid \text{ppbv h}^{-1}$ for all values of $\text{N}(\text{O}_3)$.

For EASE 97, a second set of NO_x measurements was available from an instrument designed and built at NOAA and run by the University of East Anglia (referred to hereafter as the UEA NO_{xy}). $\text{N}(\text{O}_3)$ values were recalculated both from peroxy radical measurements and from the PSS expression using the UEA NO_{xy} data (assuming $[\text{HO}_2] = 0.5[\text{HO}_2 + \text{RO}_2]$); the full time series is shown in Figure 4.14. A comparison of Figs 4.11 (b) and 4.14 shows that the $\text{N}(\text{O}_3)$ values calculated from the peroxy radical data were generally shifted down slightly when the UEA NO_{xy} data were used in place of the CRANOX data. Indeed, some days with small net ozone destruction were now observed. However, the opposite was generally the case for the PSS calculated $\text{N}(\text{O}_3)$ values: there were now no days of net ozone destruction observed during EASE 97 using this method. Figure 4.15 is a scatter plot of the EASE 97 $\text{N}(\text{O}_3)$ values calculated from peroxy radical measurements (Equation 4.12) using the two sets of NO data. The degree of correlation is very good ($r^2 = 0.94$), although the values calculated from the UEA NO_{xy} NO data were systematically $ca \mid 25\% \mid$ lower than those calculated from the CRANOX data.

Figure 4.14 Daytime mean ozone tendencies calculated for EASE 97 using the UEA NO_{xy} instrument NO data

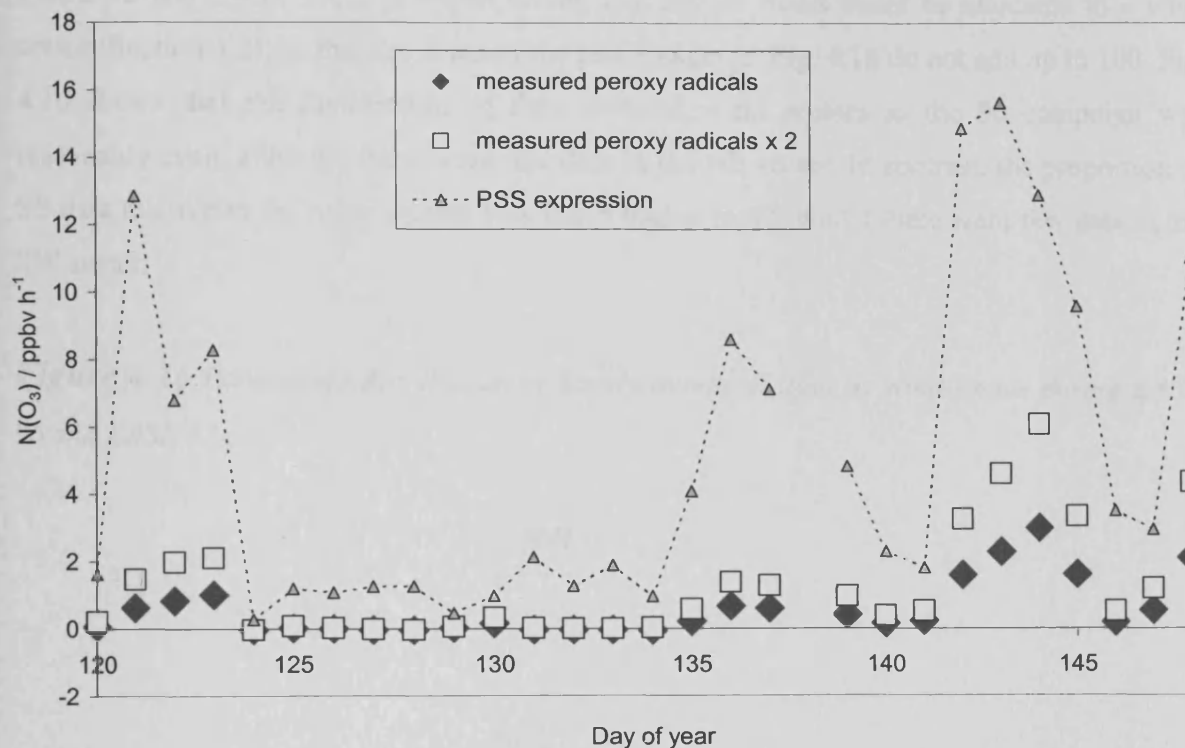
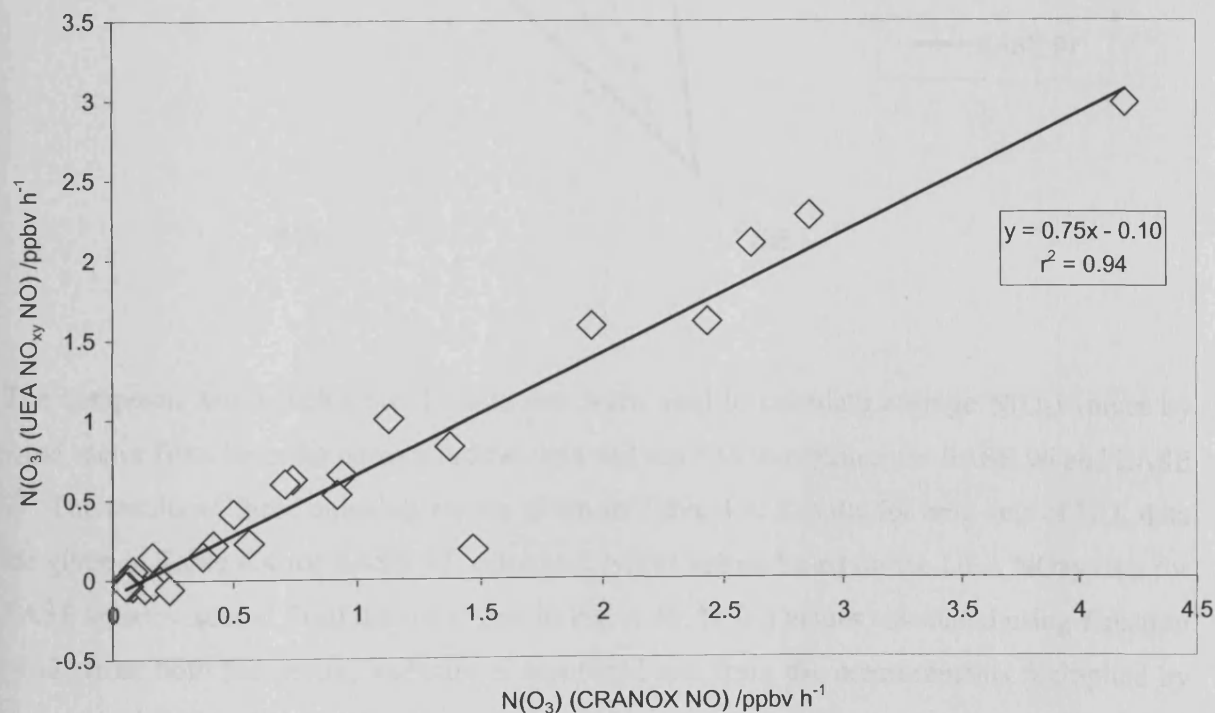


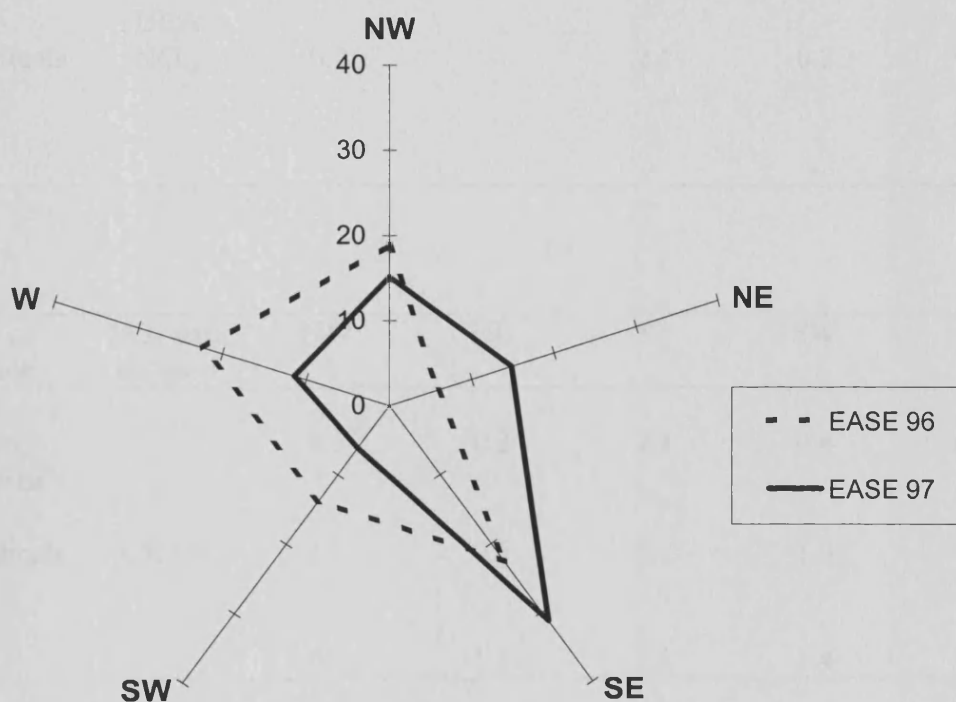
Figure 4.15 Scatter plot of daytime mean ozone tendencies calculated from Equation (4.12) for EASE 97 using CRANOX and UEA NO_{xy} NO data



4.5.2 Wind sector comparison

Figure 4.16 shows the distribution of hourly averaged data between the wind sectors for EASE 96 and EASE 97; it is worth noting that not all hours could be allocated to a wind sector (Section 4.2), so that the sums of the percentages in Fig. 4.16 do not add up to 100. Fig. 4.16 shows that the distribution of data between wind sectors in the 96 campaign was reasonably even, although there were few data in the NE sector. In contrast, the proportion of SE data relative to the other sectors was much higher in 97, whilst there were few data in the SW sector.

Figure 4.16 Percentage distribution of hourly averaged data by wind sector during EASE 96 and EASE 97



The composite wind sector hourly data sets were used to calculate average $N(O_3)$ values by wind sector from both the peroxy radical data and the PSS expression for EASE 96 and EASE 97. The results of these calculations are given in Table 4.4. Results for both sets of NO_x data are given in Table 4.4 for EASE 97; estimated $N(O_3)$ values based on the UEA NO_{xy} data for EASE 96 were scaled from the trend-line in Fig. 4.15. $N(O_3)$ values calculated using Equation (4.12) from both the peroxy radicals as measured and from the measurements multiplied by two are included in Table 4.4.

Table 4.4 Mean daytime (06:00-19:00) ozone tendency ($N(O_3)$) values by wind sector^a

(a) EASE 96

Method of calculation	NO _x data set used	NW	NE	SE	SW	W
Measured peroxy radicals		0.1	-	1.4	0.2	0.2
Peroxy radicals x 2	CRAN	0.4	-	3.0	0.5	0.5
PSS		6.8	-	-2.6	3.0	0.2
Measured peroxy radicals ^b		0.0	-	0.9	0.0	0.0
Peroxy radicals x 2 ^b	UEA NO _{xy}	0.2	-	2.1	0.3	0.3
PSS		-	-	-	-	-

(b) EASE 97

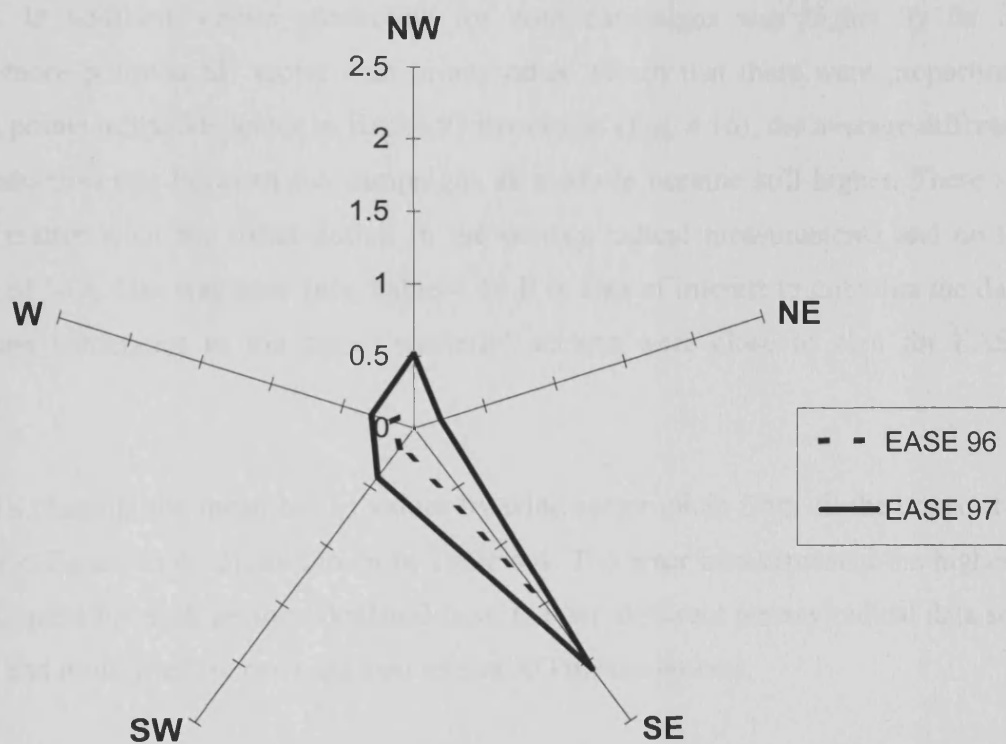
Method of calculation	NO _x data set used	NW	NE	SE	SW	W
Measured peroxy radicals		0.5	0.2	2.1	0.4	0.3
Peroxy radicals x 2	CRAN	1.1	0.5	4.2	1.0	0.7
PSS		0.7	1.1	7.3	1.4	1.8
Measured peroxy radicals		0.2	0.0	1.7	0.3	0.1
Peroxy radicals x 2	UEA NO _{xy}	0.4	0.1	3.6	0.6	0.3
PSS		2.9	2.7	9.6	2.6	3.3

^a Units are ppbv h⁻¹.^b These values are scaled from the CRANOX values based on the NO_{xy}/CRANOX $N(O_3)$ ratio obtained from the EASE 97 data.

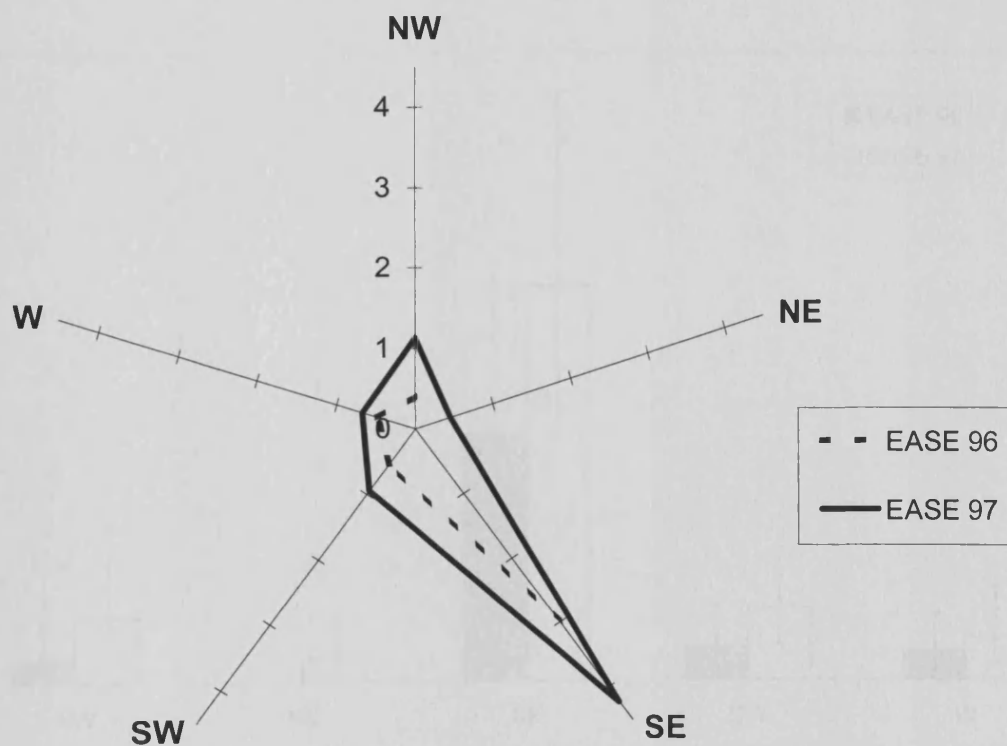
Figures 4.17 (a) and (b) show the average $N(O_3)$ values by wind sector based on (a) the peroxy radicals as measured and (b) the peroxy radical measurements multiplied by two (both

Figure 4.17 Mean daytime ozone tendencies calculated from peroxy radical measurements for EASE 96 and EASE 97 by wind sector (ppbv h^{-1})

(a) Peroxy radicals as measured



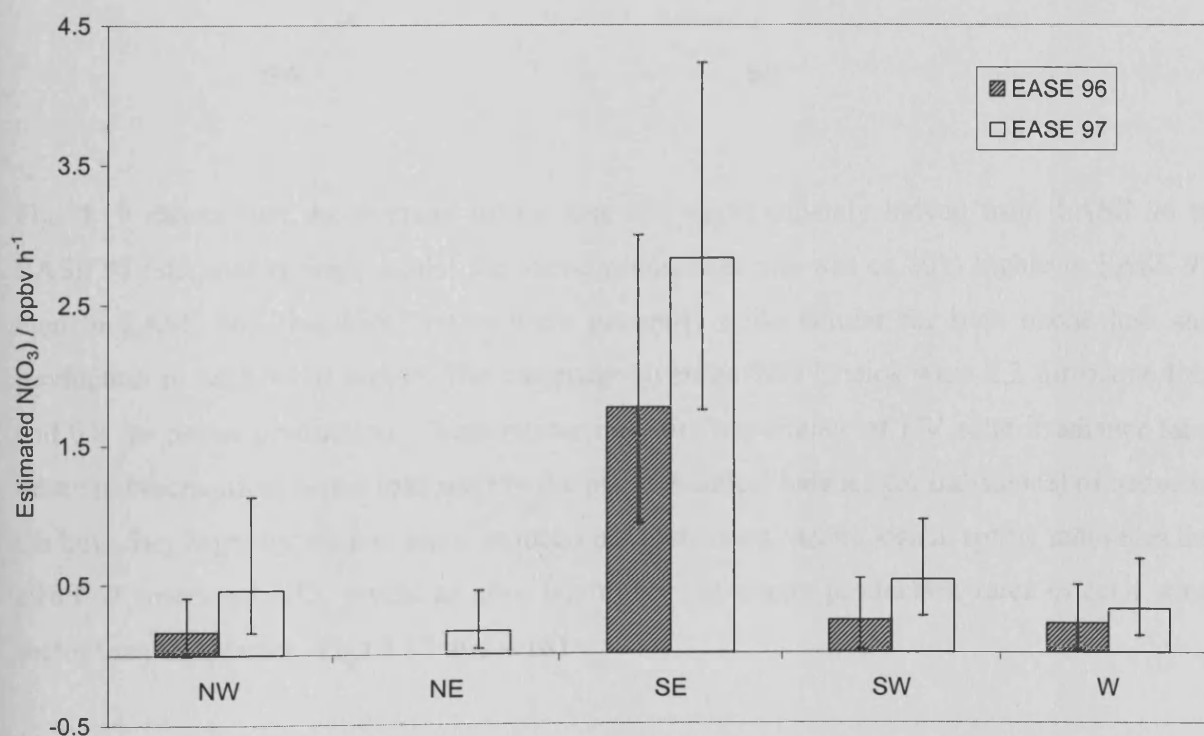
(b) Peroxy radicals multiplied by two



calculated from Equation (4.12) and using the CRANOX NO data). Clearly the calculated $N(O_3)$ values for the measured peroxy radicals multiplied by two were considerably greater than for the peroxy radicals as measured. Nevertheless, Figs 4.17 (a) and (b) show that ozone production rates were greater for all wind sectors in EASE 97 (spring) than in EASE 96 (summer). In addition, ozone production for both campaigns was higher by far in the generally more polluted SE sector than in any other. Given that there were proportionately more data points in the SE sector in EASE 97 than in 96 (Fig. 4.16), the average difference in ozone production rate between the campaigns as a whole became still higher. These results apply no matter what the exact deficit in the peroxy radical measurements and no matter which set of NO_x data was used (see Table 4.4). It is also of interest to note that the daytime mean ozone tendencies in the three 'westerly' sectors were close to zero for EASE 96 (summer).

Figure 4.18 presents the mean $N(O_3)$ values by wind sector taken from all the peroxy radical calculations (Equation 4.12), as shown in Table 4.4. The error bars represent the highest and lowest estimates for each sector calculated from the two different peroxy radical data sets (as measured and multiplied by two) and two sets of NO measurements.

Figure 4.18 Mean daytime ozone tendency using all data combinations (see text for details) for EASE 96 and EASE 97 by wind sector



Qualitatively, the importance of the SE sector in determining the overall ozone production potential at Mace Head is clearly illustrated in Fig. 4.18. Figure 4.19 shows the 96/97 ratios of the calculated daytime mean ozone production and loss rates (ppbv h^{-1}) from Equation (4.12) by wind sector using the peroxy radical mixing ratios as measured, and an assumed HO_2/RO_2 ratio of 1.

Figure 4.19 Daytime (06:00-19:00) mean EASE 96/EASE 97 ozone production and loss rate ratios by wind sector

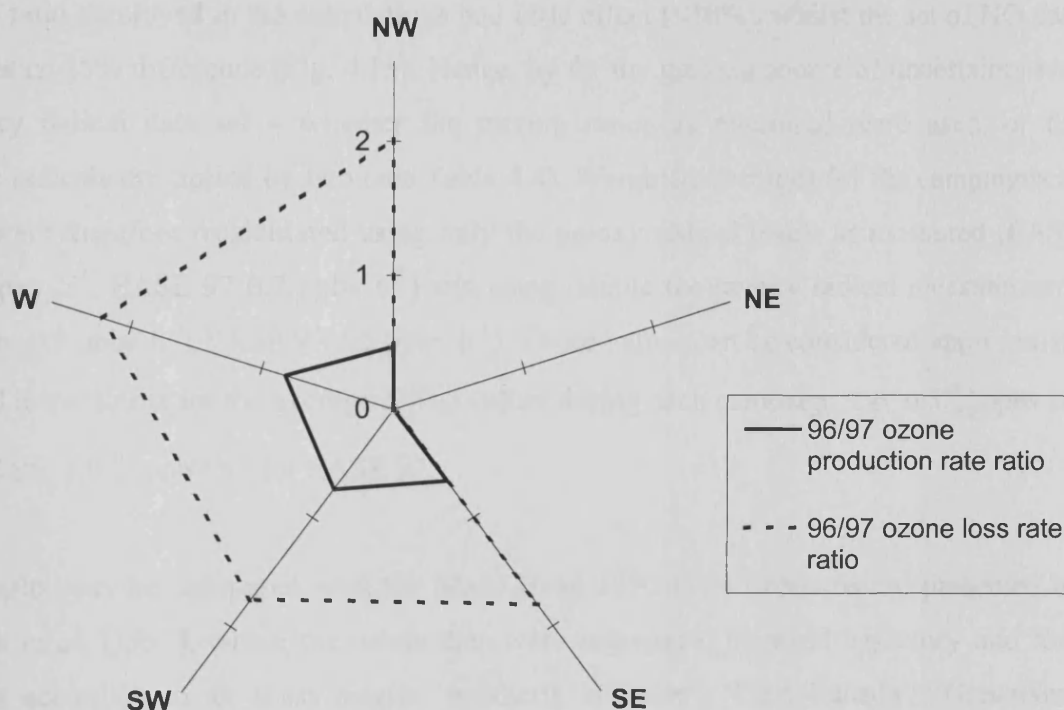


Fig. 4.19 shows that the average ozone loss rate approximately halved from EASE 96 to EASE 97 (summer/spring), whilst the ozone production rate was ca 20% higher in EASE 97 than in EASE 96. The 96/97 ratios were generally quite similar for both ozone loss and production in each wind sector. The campaign average 96/97 ratios were 2.2 for ozone loss and 0.8 for ozone production. These ratios show the importance of UV solar irradiance (and hence photochemical ozone loss rate) in the photochemical balance (or imbalance) of ozone in the boundary layer by season, since reduced photochemical ozone loss in spring redoubles the effect of increased NO_x levels to give far higher net ozone production rates in each wind sector than in summer (Figs 4.17 and 4.18).

The mean estimates for $N(O_3)$ by wind sector were used to derive weighted average $N(O_3)$ values for the whole of each campaign period: 0.5 ppbv h^{-1} for EASE 96; 1.0 ppbv h^{-1} for EASE 97. In each case, the bulk of the ozone production derived from the more polluted SE sector (79% for EASE 96, 85% for EASE 97). (These calculations neglected data hours not allocated to any wind sector.) These values would appear to be significantly different, even allowing for the sources of error described previously. Since the SE wind sector provided the greatest contribution to these $N(O_3)$ campaign estimates, it is worth considering again the possible sources of error involved in the SE values in isolation, since these errors will dominate those from other sectors. At relatively high $N(O_3)$ values, Fig. 4.13 shows that the HO_2/RO_2 ratio employed in the calculations had little effect ($<10\%$), whilst the set of NO data used made *ca* 25% difference (Fig. 4.15). Hence, by far the greatest source of uncertainty was the peroxy radical data set – whether the mixing ratios as measured were used, or the measured radicals multiplied by two (see Table 4.4). Weighted averages for the campaigns as a whole were therefore recalculated using only the peroxy radical levels as measured (EASE 96: 0.3 ppbv h^{-1} ; EASE 97 0.7 ppbv h^{-1}) and using double the peroxy radical measurements (EASE 96: 0.8 ppbv h^{-1} ; EASE 97 1.5 ppbv h^{-1}). These values can be considered approximate upper and lower limits for the average $N(O_3)$ values during each campaign, *i.e.* $0.5^{+0.3}_{-0.2} \text{ ppbv h}^{-1}$ for EASE 96, $1.0^{+0.5}_{-0.3} \text{ ppbv h}^{-1}$ for EASE 97.

These results may be compared with the Mace Head 1990-1994 ozone record presented by *Simmonds et al.* [1997], where the ozone data were segregated by wind trajectory into four categories according to air mass origin: 'southerly latitudes'; 'USA-Canada'; 'Greenland-Iceland'; and 'Europe'; and the possible role of *in-situ* photochemistry discussed in qualitative terms. An ozone excess over the estimated Northern Hemisphere mid-latitude background (NHMLB) $[O_3]$ value of 34.8 ppbv was observed by *Simmonds et al.* [1997] for each air mass except 'southerly latitudes' in spring (March-May) for the period 1990-1994. Table 4.4 and Fig. 4.18 show that for EASE 97 (April-May 1997), net ozone production was observed in all wind sectors. In contrast, for the summer period (July-August 1990-1994), an ozone deficit with respect to the NHMLB was observed by *Simmonds et al.* [1997] for all air masses except 'Europe', where a small excess was noted. Table 4.4 and Fig. 4.18 show that for EASE 96 (July-August 1996), ozone production and destruction processes were closer to being in balance in all except the SE wind sector, where significant net ozone production was observed. The higher average ozone production rate in spring compared to summer points to the importance of tropospheric photochemistry in driving the widely reported spring ozone maximum in the Northern Hemisphere (see *Monks* [2000], and references therein).

4.6 Ozone Compensation Point

As mentioned in Chapter 1, the *ozone compensation point* is commonly defined as the mixing ratio of NO required to balance photochemical ozone production and destruction in the troposphere, *i.e.*, $N(O_3) = 0$. *Carpenter et al.* [1997] estimated an ozone compensation point of 55 ± 30 pptv NO for Mace Head based on data collected during the Atlantic Atmospheric Photochemistry Experiment (ATAPEX) campaign in May 1995. *Zanis et al.* [2000b] estimated a compensation point of 24 ± 9 pptv NO for the Jungfraujoch in Switzerland by plotting the daily averaged $N(O_3)$ values calculated from measured peroxy radicals *versus* the daily averaged NO/O₃ ratios. The compensation point was then estimated by multiplying the intercept of this plot by the campaign averaged ozone mixing ratio. $N(O_3)$ values of more than 2 ppbv h⁻¹ were excluded from the analysis due to the non-linearity of ozone production at high [NO]. Figure 4.20 shows the results of a similar approach for (a) EASE 96, (b) EASE 97. In each case, the CRANOX NO data and the peroxy radical data as measured were used to calculate $N(O_3)$ from Equation (4.12). Fig. 4.20 yielded compensation points of 35 ± 30 pptv NO for EASE 96 and 42 ± 21 pptv NO for EASE 97. The same procedure was followed using the UEA NO_{xy} NO data for EASE 97, and also the measured peroxy radicals multiplied by two for both campaigns. The results are collected in Table 4.5.

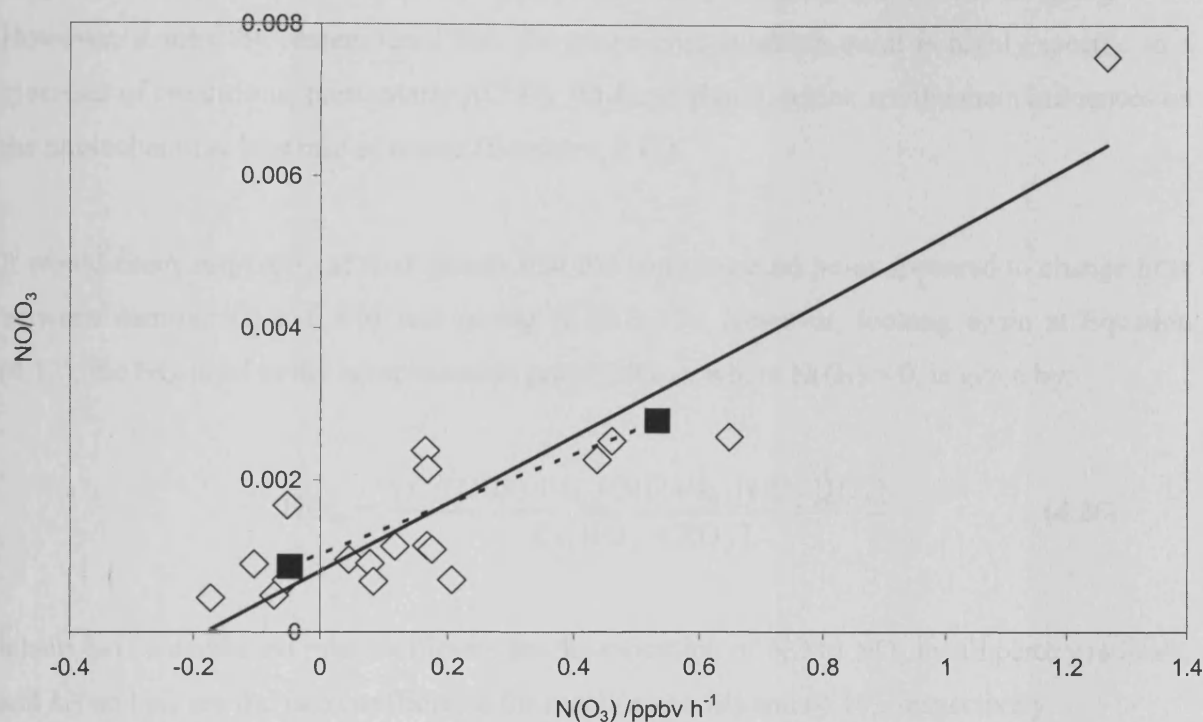
Table 4.5 Ozone compensation points ($N(O_3)$) for EASE 96 and 97 estimated by plotting the daily averaged $N(O_3)$ values calculated from measured peroxy radicals *versus* the daily averaged NO/O₃ ratio

Data sets used	EASE 96 ^a	EASE 97 ^a
CRANOX NO; measured peroxy radicals	35 (30)	42 (21)
CRANOX NO; peroxy radicals x 2	18 (13)	34 (18)
UEA NO _{xy} NO; measured peroxy radicals	-	39 (17)
UEA NO _{xy} NO; peroxy radicals x 2	-	11 (8)

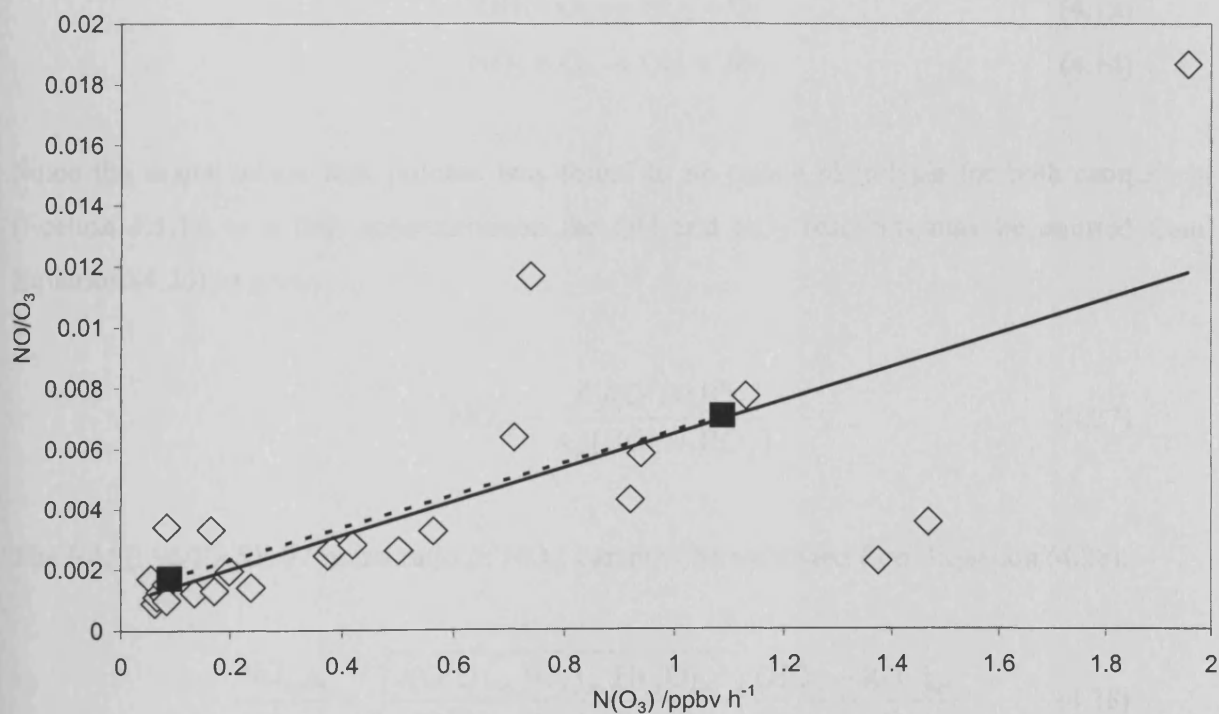
^a Compensation points are in pptv [NO]; values in brackets are 1σ values based on the standard errors of conventional linear regression fits to the data.

Figure 4.20 Scatter plots of mean daytime $N(O_3)$ versus NO/O_3 for EASE 96 and EASE 97^a

(a) EASE 96



(b) EASE 97



^a These Figures use CRANOX NO_x and $N(O_3)$ values from the measured peroxy radicals. The solid lines represent the standard linear regression lines of best fit to the data; the dashed lines with filled squares are the lines of best fit using the organic correlation method, which takes into account errors in both dependent and independent variables [e.g., *Zanis et al.*, 2000b]. The latter line is used to derive estimates for the ozone compensation point ($N(O_3) = 0$; see text for details).

The mean estimates from all data combinations were 27 ± 22 pptv NO for EASE 96 and 32 ± 16 pptv NO for EASE 97. It is interesting to note that these values are at the lower extreme of the range (55 ± 30 pptv NO) obtained by *Carpenter et al.* [1997] for Mace Head in spring 1995. However, it must be remembered that the ozone compensation point is highly specific to a given set of conditions, particularly $j(\text{O}^1\text{D})$, $[\text{O}_3]$ and $[\text{H}_2\text{O}]$, which are the main influences on the photochemical loss rate of ozone (Equation 4.12).

It would seem surprising at first glance that the compensation point appeared to change little between summer (EASE 96) and spring (EASE 97). However, looking again at Equation (4.12), the NO level at the compensation point (NO_{cp}), where $\text{N}(\text{O}_3) = 0$, is given by:

$$\text{NO}_{\text{cp}} = \frac{\{f \cdot j(\text{O}^1\text{D}) + k_{13}[\text{OH}] + k_{14}[\text{HO}_2]\}[\text{O}_3]}{k_p[\text{HO}_2 + \text{RO}_2]} \quad (4.26)$$

where k_p is a combined rate coefficient for the oxidation of NO to NO_2 by all peroxy radicals, and k_{13} and k_{14} are the rate coefficients for reactions (4.13) and (4.14), respectively.



Since the major ozone loss process was found to be ozone photolysis for both campaigns (Section 4.5.1), to a first approximation the OH and HO_2 reactions may be omitted from Equation (4.26) to give:

$$\text{NO}_{\text{cp}} \sim \frac{f \cdot j(\text{O}^1\text{D}) \cdot [\text{O}_3]}{k_p[\text{HO}_2 + \text{RO}_2]} \quad (4.27)$$

The EASE 96/EASE 97 mean ratio of NO_{cp} can now be estimated from Equation (4.28):

$$\frac{\text{NO}_{\text{cp}96}}{\text{NO}_{\text{cp}97}} = \sqrt{\frac{j(\text{O}^1\text{D})_{96} \cdot [\text{O}_3]_{96} \cdot [\text{H}_2\text{O}]_{96}}{j(\text{O}^1\text{D})_{97} \cdot [\text{O}_3]_{97} \cdot [\text{H}_2\text{O}]_{97}}} * \frac{[\text{HO}_2 + \text{RO}_2]_{97}}{[\text{HO}_2 + \text{RO}_2]_{96}} \quad (4.28)$$

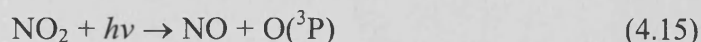
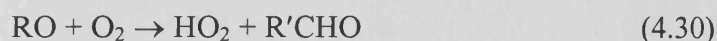
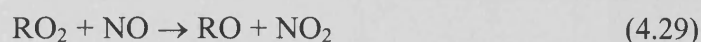
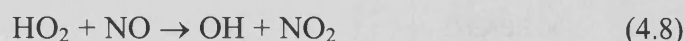
assuming that the other terms in f and k_p are invariant with season. As already noted in Section 4.4, the campaign mean ratios on the right-hand side of Equation (4.28) were 1.32 and

$1/1.42 = 0.70$, respectively, which gives an estimated 96/97 NO_{cp} ratio of 0.9. Although this calculation is only approximate, it does lend some credence to the finding presented here that the ozone compensation points in EASE 96 and EASE 97 were very similar. Nevertheless, the scatter evident in Fig. 4.20 and the large error ranges in the NO_{cp} estimates for both campaigns show the difficulty inherent in estimating the ozone compensation point with precision (see also Chapter 5, Section 5.5.3).

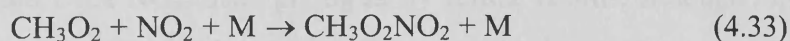
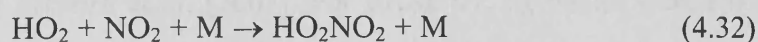
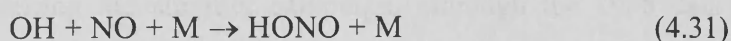
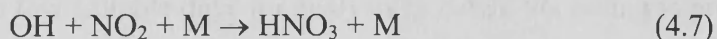
4.7 Ozone Production Efficiency

4.7.1 Calculation of ozone production efficiency

The production of ozone in the troposphere can be summarised by the following sequence of reactions:



Since NO is regenerated by photolysis of NO_2 , no net change in NO_x occurs in this ozone production sequence. There are competing reactions, however, in which NO_x molecules are oxidised to a form in which they cannot take part in the ozone production cycle, including the following:



As described in Chapter 1, the *ozone production efficiency* (E_N) in the troposphere is usefully defined as the number of molecules of ozone produced per molecule of NO_x oxidised to an NO_z species [Liu *et al.*, 1987], where $\text{NO}_z = \text{NO}_y - \text{NO}_x$, and is given by:

$$E_N = \frac{\Delta O_3}{\Delta(\text{NO}_y - \text{NO}_x)} \quad (4.34)$$

E_N values were obtained from standard linear regression plots of daytime (06:00-19:00 GMT) $[\text{O}_3]$ versus $[\text{NO}_z]$ ($= \text{NO}_y - \text{NO}_x$) for each day during both EASE 96 and EASE 97 where full days of data were available. The resulting ozone production efficiencies are plotted against daytime mean $[\text{NO}_x]$ in Figure 4.21.

Figure 4.21 Ozone production efficiency (E_N) as a function of daytime mean $[\text{NO}_x]$ during EASE 96 and EASE 97

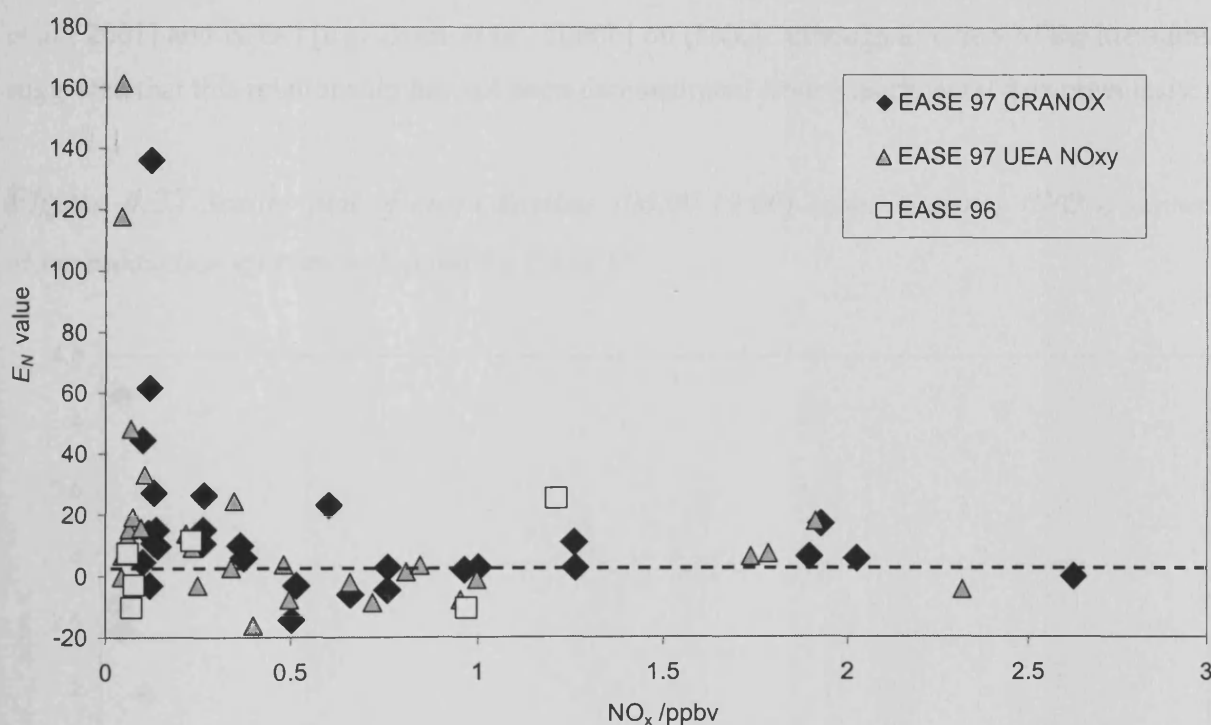


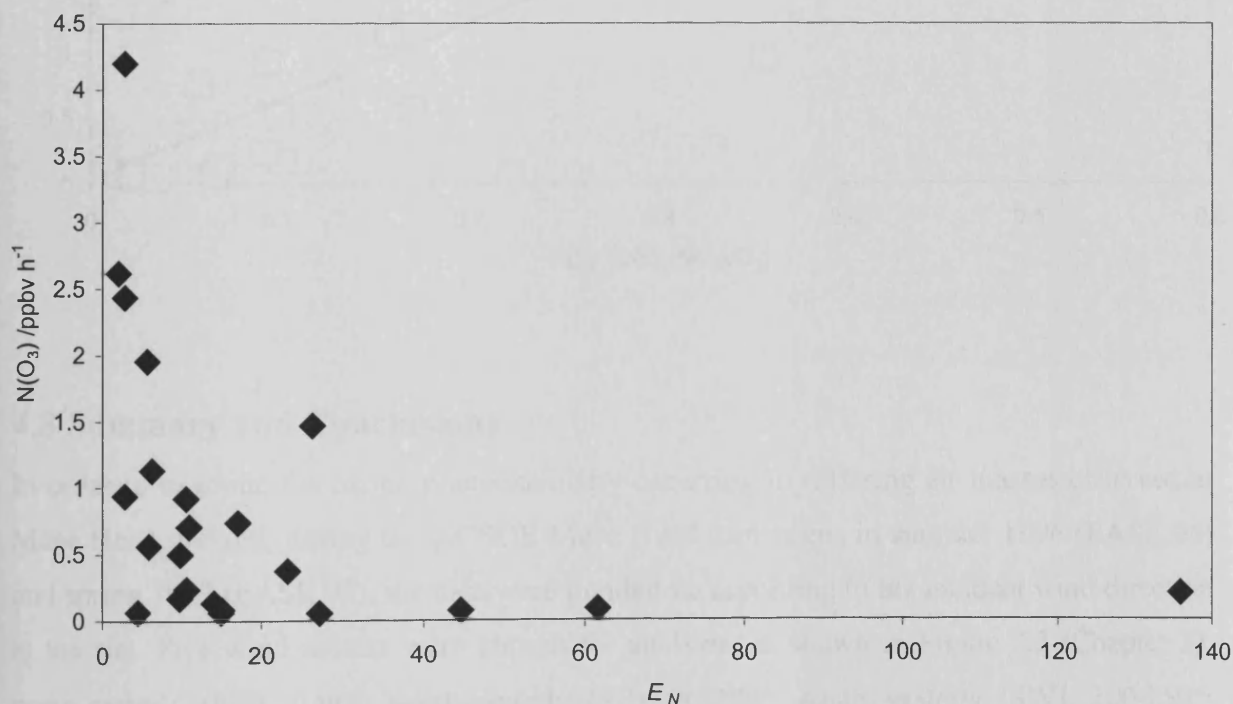
Fig. 4.21 shows that there were few suitable days for analysis in EASE 96, owing to problems with the NO_y measurements during the summer campaign, although the 1996 data set is considered in more detail by Rickard *et al.* [2001]. For EASE 97, E_N values were calculated using both the CRANOX and UEA NO_{xy} data, giving fairly similar results, although Fig. 4.21 shows that the observed daytime NO_x mixing ratios were generally lower as measured by the UEA NO_{xy} instrument, as discussed in Section 4.5.1 (see also Fig. 4.15). The most striking feature of Fig. 4.21 is the strong anti-correlation between E_N and NO_x , implying that ozone is produced very efficiently at low NO_x , where the net ozone production rate is relatively small, whereas at high NO_x , where the ozone production rate is high (*i.e.*, the ozone tendency is strongly positive) the ozone production efficiency is relatively small. Fig. 4.21 also shows that

at high NO_x , ozone production efficiency is relatively insensitive to changes in NO_x , *i.e.*, that ozone production in these conditions is approaching VOC limitation (see also Chapter 1). Similar results have been obtained previously [*e.g.*, Liu *et al.*, 1987; Carpenter *et al.*, 2000], although few studies of ozone production efficiency have been made in the marine boundary layer [Rickard *et al.*, 2001].

4.7.2 Ozone production efficiency and ozone tendency

Figure 4.22 shows a scatter plot of daily mean daytime values of ozone tendency ($N(\text{O}_3)$) and E_N for EASE 97, where days with negative E_N have been excluded from the analysis. A distinct anti-correlation between the two variables is immediately apparent in Fig. 4.22: this is not surprising, given the strong dependence of both E_N [*e.g.*, Carpenter *et al.*, 2000; Rickard *et al.*, 2001] and $N(\text{O}_3)$ [*e.g.* Zanis *et al.*, 2000b] on $[\text{NO}_x]$, although a review of the literature suggested that this relationship has not been demonstrated from experimental data previously.

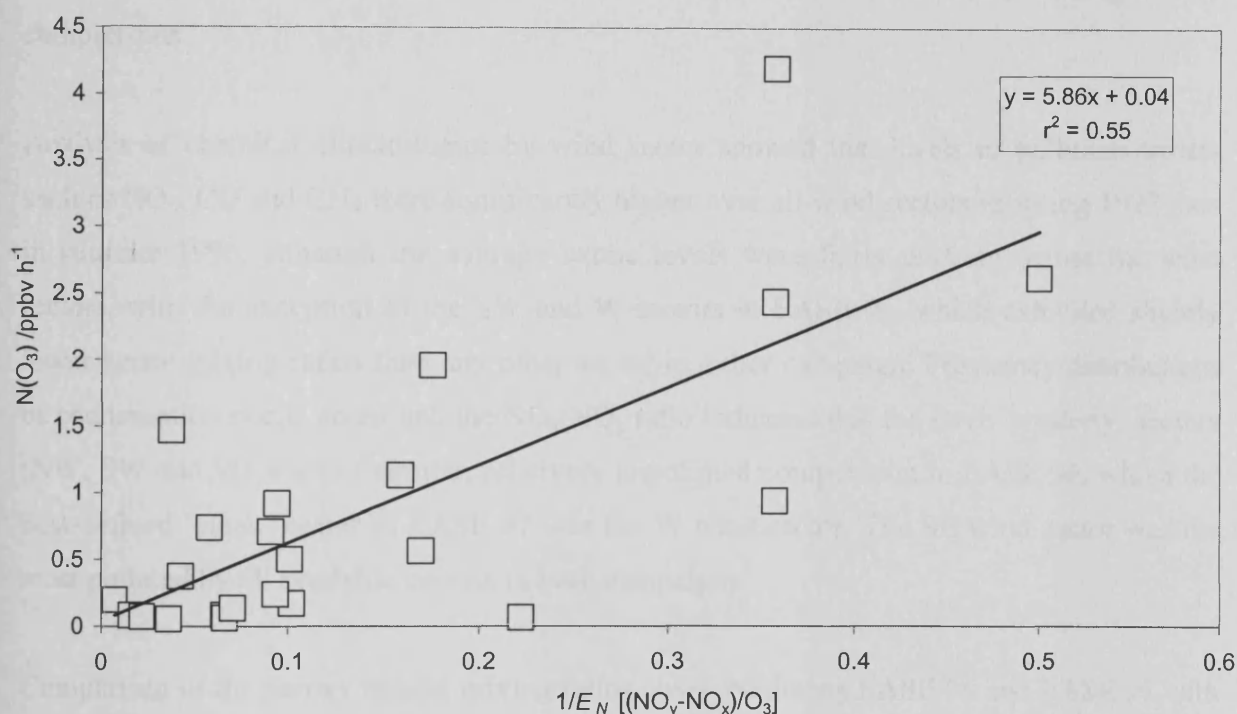
Figure 4.22 Scatter plot of mean daytime (06:00-19:00) ozone tendency ($N(\text{O}_3)$) versus ozone production efficiency (E_N) during EASE 97



The important things to note from Fig. 4.22 are: first, at high ozone tendencies, the efficiency of ozone production is low; second, where E_N is large, *i.e.* ozone production efficiency is high, very little ozone is actually being produced in absolute terms. Figure 4.23 shows a plot of $1/E_N$ versus $N(\text{O}_3)$, for comparison. A reasonable straight-line fit was obtained ($r^2 = 0.55$),

indicating that over 50% of the variation in ozone tendency could be explained by the variations in $[\text{NO}_x]$, $[\text{NO}_y]$ and $[\text{O}_3]$ alone during EASE 97. This allows some confidence that the ozone productivity of air masses may be estimated routinely from NO_x , NO_y and O_3 measurements, given that NO_x -limited conditions apply [e.g., Carpenter *et al.*, 1998; Rickard *et al.*, 2001].

Figure 4.23 Scatter plot of mean daytime (06:00-19:00) ozone tendency ($N(\text{O}_3)$) versus reciprocal ozone production efficiency ($1/E_N$) during EASE 97



4.8 Summary and Conclusions

In order to examine the ozone photochemistry occurring in differing air masses observed at Mace Head, Ireland, during the ACSOE Mace Head campaigns in summer 1996 (EASE 96) and spring 1997 (EASE 97), the data were divided up according to the incident wind direction at the site. Five wind sectors were chosen for analysis, as shown in Figure 3.3 (Chapter 3): north-easterly (NE), 0-90°; south-easterly (SE), 90-200°; south-westerly (SW), 200-250°; westerly (W), 250-300°; and north-westerly (NW), 300-360°. The effects of local sea/coast breezes were removed from the analysis by selecting data only where the local wind speed was over 3 m s^{-1} [cf. Cape *et al.*, 2000]. Comparison of the wind sector classification with two independent air mass classifications schemes based on the ECMWF 5-day back trajectories, developed by the University of Leeds and the Institute of Terrestrial Ecology, showed that in

the summer campaign, westerly air flow over the Atlantic, whether from the mid-Atlantic at low latitudes or originating in North America, was very significant, whereas in EASE 97 the most important air mass type was clearly polar in origin. For EASE 96, both trajectory analysis comparisons showed that the SW and W wind sectors comprised mainly westerly/south-westerly airflow off the Atlantic; the origins of the other three sectors differed according to the trajectory analysis used. For EASE 97, both comparisons showed that the W wind sector was the best-defined, although its origins were not off the Atlantic ocean as in summer 1996, but from the Arctic. The highest contributions from semi-polluted UK/continental air were found to be in the NW, NE and SE wind sectors according to both comparisons.

Analysis of chemical climatologies by wind sector showed that levels of pollution tracers such as NO_x , CO and CH_4 were significantly higher over all wind sectors in spring 1997 than in summer 1996, although the average ozone levels were fairly uniform across the wind sectors, with the exception of the SW and W sectors in EASE 96, which exhibited slightly lower ozone mixing ratios than any other sector in either campaign. Frequency distributions of condensation nuclei count and the NO_x/NO_y ratio indicated that the three 'westerly' sectors (NW, SW and W) were of similar, relatively unpolluted composition in EASE 96, whilst the best-defined 'clean' sector in EASE 97 was the W wind sector. The SE wind sector was the most polluted by all available criteria in both campaigns.

Comparison of the peroxy radical mixing ratios observed during EASE 96 and EASE 97 with the expected 96/97 ratios calculated using the low- NO_x steady-state approximation of Penkett *et al.* [1997] showed a reasonable level of agreement (campaign daytime mean measured ratio 1.4, mean calculated ratio 1.3), although the comparison gave better results using the campaign-averaged data rather than using the W wind sector data only, contrary to expectation. This anomaly could be a result of higher $[\text{NO}_x]$ and CO/ CH_4 ratios in the spring campaign; the summer-spring change in both quantities was greater in the W wind sector than over the campaigns as a whole.

Calculation of photochemical ozone tendencies using both *in-situ* peroxy radical measurements and the deviation from photochemical stationary state (PSS) gave qualitative agreement. However, the PSS-derived estimates were *ca* three times higher than those derived from peroxy radical measurements, on average. This result is in qualitative accord with previous work by Cantrell *et al.* [1997a], where peroxy radical mixing ratios estimated from

PSS perturbation exceeded measured levels by a factor of two; and by *Carpenter et al.* [1998], where peroxy radical mixing ratios estimated from PSS perturbation were found to exceed measured and modelled peroxy radical levels by up to two orders of magnitude. This effect was attributed by *Carpenter et al.* [1998] to the high sensitivity of the PSS expression to errors in individual measurements. The absolute magnitude of the error in the $N(O_3)$ calculations attributable to the HO_2/RO_2 ratio employed was estimated to be less than *ca* 0.1 ppbv h^{-1} for all values of $N(O_3)$.

Analysis of ozone tendency by wind sector showed that the overall ozone production at Mace Head was dominated by polluted air masses originating in Britain and continental Europe for both summer 1996 and spring 1997 (SE wind sector). The proportion of such polluted air masses encountered at Mace Head was much greater in the spring than in the summer; this effect appears to be a regular feature of the climatology of this coastal site [*Derwent et al.*, 1998]. In addition, the ozone tendency was greater for each wind sector in spring 1997 than in summer 1996. These two factors combined to ensure that the average ozone production rate was two times higher for spring 1997 than for summer 1996: $0.5^{+0.3}_{-0.2}$ ppbv h^{-1} for EASE 96, $1.0^{+0.5}_{-0.3}$ ppbv h^{-1} for EASE 97. The error limits are estimates based on the instrumental uncertainties of the PERCA [HO_2+RO_2] and radiometric $j(O^1D)$ measurements, and allow for the likely magnitude of the humidity effect on the PERCA measurements (see Chapters 2 and 6). The averaged ozone production rates show the importance of urban plumes to the ozone budget of remote locations, and strongly suggest that the Northern Hemisphere spring ozone maximum is controlled, at least in part, by *in-situ* photochemistry [*Monks*, 2000].

The mean estimates of the ozone compensation point ($N(O_3)=0$) were 27 ± 22 pptv NO for EASE 96 and 32 ± 16 pptv NO for EASE 97. Although the similarity of these values in different seasons might seem surprising at first glance, examination of the expression for ozone tendency (Equation 4.12) showed that the campaign mean 96/97 compensation point ratio would be expected to be *ca* 0.9. Both the values obtained in the present work are at the lower extreme of the range 55 ± 30 pptv NO estimated by *Carpenter et al.* [1997] for Mace Head in spring 1995 during the ATAPEX campaign.

The ozone production efficiency, defined as the number of molecules of ozone produced per molecule of NO_x oxidised to an NO_z species, showed a strong inverse dependence on $[NO_x]$, as reported previously [*e.g.*, *Liu et al.*, 1987; *Carpenter et al.*, 2000], showing that ozone is produced very efficiently at low NO_x , where the net ozone production rate is relatively small,

whereas at high NO_x , where the ozone production rate is high (*i.e.*, the ozone tendency is strongly positive) the ozone production is relatively small. A reasonable straight-line fit was obtained in a scatter plot of $1/E_N$ versus ozone tendency ($r^2 = 0.55$), indicating that over 50% of the variation in ozone tendency could be explained by consideration of $[\text{NO}_x]$, $[\text{NO}_y]$ and $[\text{O}_3]$ alone during EASE 97. This allows some confidence that the ozone productivity of air masses may be estimated routinely from NO_x , NO_y and O_3 measurements, given that NO_x -limited conditions apply [*e.g.*, Carpenter *et al.*, 1998; Rickard *et al.*, 2001].

Chapter 5 - The SOAPEX 2 Experiment: Cape Grim, January-February 1999

5.1 Introduction

5.1.1 Background to the SOAPEX campaigns

As discussed in Chapters 1 and 4, peroxy radicals produced in the reactions of the hydroxyl (OH) radical with CO, CH₄ and NMHCs (non-methane hydrocarbons) are important intermediates in both the production and destruction of tropospheric ozone. The tendency of the atmosphere to produce or destroy ozone overall is a non-linear function dependent on the availability of NO_x and NMHCs. In low-NO_x conditions, prevalent in much of the Southern Hemisphere remote marine boundary layer (MBL), ozone is chemically removed, predominately by the following reactions:



Even at low [NO_x], however, there is a small positive contribution to the photochemical ozone budget from the photolysis of NO₂. These photochemical pathways are coupled to physical processes, which also affect the observed ozone concentrations: deposition to the available surfaces, and entrainment from the free troposphere. The sum of these processes may be represented in the form of the ozone continuity equation [after *Graedel and Crutzen*, 1993]:

$$\frac{d[\text{O}_3]}{dt} = N(\text{O}_3) + \frac{E_v([\text{O}_3]_{\text{ft}} - [\text{O}_3])}{H} + \frac{v_d[\text{O}_3]}{H} \quad (5.4)$$

where $N(\text{O}_3)$ is the photochemical ozone tendency (the net result of production, $P(\text{O}_3)$, and destruction, $L(\text{O}_3)$ – see Chapter 4), E_v is the entrainment velocity[†], $[\text{O}_3]_{\text{ft}}$ is the concentration of free-tropospheric ozone, v_d is the dry deposition velocity and H is the height of the

[†] Recently *de Laat and Lelieveld* [2000] have questioned the importance of this term in the ozone budget of the marine boundary layer, suggesting that photochemistry and advection can explain the observed ozone diel cycle.

boundary layer. The remote MBL has been proven to represent a net sink for ozone during several ocean studies, including previous work at Cape Grim [Ayers *et al.*, 1992]; photochemical destruction is now known to be the primary component of this sink [e.g., Johnson *et al.*, 1990; Thompson *et al.*, 1993; Slemr and Tremmel, 1994; Brémaud and Taupin, 1998].

As outlined in Chapter 1, the first Southern Ocean Atmospheric Photochemistry Experiment (SOAPEX 1) campaigns took place in 1995, at the Cape Grim Baseline Atmospheric Pollution Station (CGBAPS) in Tasmania, Australia (Section 5.1.2). The main aim of these experiments was to examine in detail the photochemistry occurring in very clean (*baseline*) air masses arriving at CGBAPS off the Southern Ocean – air masses likely to have had no contact with land, and therefore anthropogenic pollution sources, for several weeks or more.

5.1.2 Measurement site

CGBAPS is located at 40°40'56" S, 144°41'18" E, on the north-western tip of Tasmania (Figure 5.1); the station is situated on the seaward edge of Cape Grim, at 94 m altitude and about the same horizontal distance from the high-water mark. An extensive program of atmospheric chemistry and meteorological measurements has been conducted at the site since 1976; details of the ongoing CGBAPS measurement programs, tabulations of data, and annual summaries of CGBAPS research and meteorological information are provided in the CGBAPS annual report series [*Baseline Atmospheric Program, Australia, 1976-1996*]. The measurement site is described in more detail by Bates *et al.* [1998] and the CGBAPS annual report series [*Baseline Atmospheric Program, Australia, 1976-1996*].

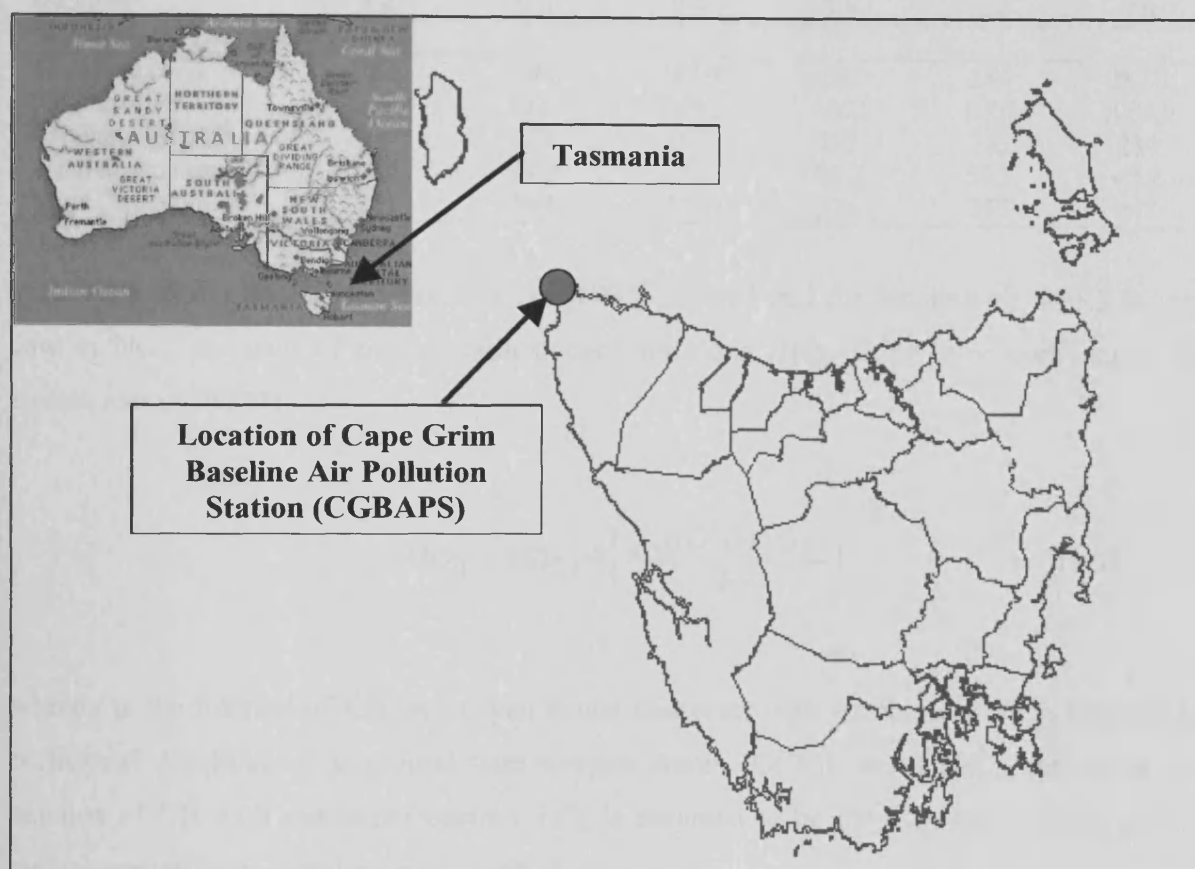
5.1.3 Comparison of SOAPEX 1a and 1b[†]

For SOAPEX 1a and 1b, baseline periods were defined using the criteria developed previously for CGBAPS: first, the wind direction must be in the sector 190-280°; second, the condensation nuclei (CN) particle count must be $<600 \text{ cm}^{-3}$ [Ayers and Gras, 1983]. During SOAPEX 1a, which took place between 24th January and 24th February 1995 (*i.e.*, during austral summer), baseline periods made up 20% of the entire data set [Monks *et al.*, 1998]. During SOAPEX 1b, which took place between 7th August and 8th September 1995 (*i.e.*, during austral winter), baseline periods made up 30% of the data set [Monks *et al.*, 2000]. In each case, a baseline hour was defined as one possessing more than 95% baseline minutes; each baseline hour was then used to build up an averaged baseline diel cycle of all

[†] The work presented in this section is described in more detail by Monks *et al.* [2000].

measurements. This baseline-averaging method has been shown to be a valid procedure by Ayers *et al.* [1996], and has the advantage that stochastic variability evident in some daily profiles, perhaps due to the vagaries of transport and/or other meteorological factors, is much reduced in the composite profiles. Table 5.1 shows the average baseline values for a number of chemical and climatological quantities for both the SOAPEX 1a and 1b campaign periods.

Figure 5.1 Map of Tasmania showing the location of Cape Grim Baseline Air Pollution Station



The measured seasonal MBL ozone record at Cape Grim [Galbally *et al.*, 1996; Ayers *et al.*, 1997], in common with other remote sites in the Southern Hemisphere [e.g., Oltmans *et al.*, 1994], exhibits a summer minimum and a winter maximum. The data in Table 5.1 show that there was approximately a doubling in the ozone mixing ratios between summer and winter in 1995, indicative of the longer atmospheric lifetime of ozone during winter. This increase in ozone with season was accompanied by an increase in both average carbon monoxide (up by *ca* 22 ppbv) and in average methane (up by *ca* 26 ppbv) mixing ratios. The average winter temperature was 5.9 K cooler than in summer: the small relative change reflects the oceanic nature of the site. The diel profile in temperature showed a range of about ± 2 K in both

summer and winter, indicative of the small diel cycle in surface heat flux over the ocean. The average atmospheric pressure was 4.3 hPa lower in winter than in summer.

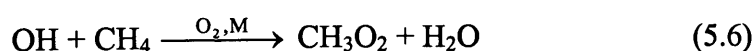
Table 5.1 Comparison of the baseline trace gas concentrations and meteorological parameters for SOAPEX 1a and 1b

Quantity	SOAPEX 1a			SOAPEX 1b		
	Min.	Max.	Mean	Min.	Max.	Mean
Trace Gases						
Ozone /ppbv	14.3	17.5	15.9	30.2	33.3	31.7
CO /ppbv	38	47	44	-	-	66.5
CH ₄ /ppbv	1658	1672	1666	-	-	1692
H ₂ O/g m ⁻³	8.4	9.6	9.0	7.9	8.2	7.9
Meteorological Parameters						
Temperature /K	286	290	287.9	281	284	282.0
Pressure /hPa	1006	1011	1009.3	1002	1007	1005.0
CN /particles cm ⁻³	214	347	297	202	265	234
Wind Speed /km h ⁻¹	22.5	35.9	29.9	38.2	50.1	42.2
Wind Direction /°	221	244	233	236	255	247

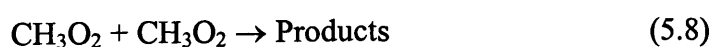
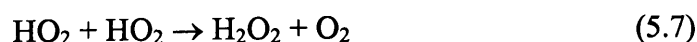
As discussed in Chapter 4, Penkett *et al.* [1997] showed that for baseline air, which is very low in NO_x, the sum of peroxy radical concentrations [HO₂+RO₂] is proportional to the square root of $j(\text{O}^1\text{D})$:

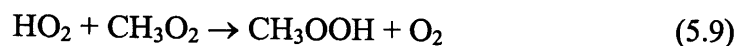
$$[\text{HO}_2 + \text{RO}_2] = \left(\frac{f \cdot j(\text{O}^1\text{D}) \cdot [\text{O}_3]}{k'} \right)^{1/2} \quad (5.5)$$

where f is the fraction of singlet oxygen atoms that react with water, rather than undergoing collisional deactivation to ground-state oxygen atoms (O(³P)), and CH₃O₂, formed in the reaction of OH with methane (reaction 5.6), is assumed to be the dominant organic peroxy radical present [*e.g.*, Carslaw *et al.*, 1999a].



The quantity denoted k' is a composite rate constant for the peroxy radical self- and cross-reactions:





and is given by:

$$k' = \frac{\beta^2 k_7 + \beta k_9 + k_8}{(\beta + 1)^2} \quad (5.10)$$

where k_1 is the rate coefficient for the reaction (5.i) and $[\text{HO}_2] = \beta[\text{CH}_3\text{O}_2]$ [Monks *et al.*, 1998]. Equation (5.5) can be used to derive the following expression for the ratio of peroxy radical concentrations summer/winter:

$$\frac{[\text{HO}_2 + \text{RO}_2]_{\text{summer}}}{[\text{HO}_2 + \text{RO}_2]_{\text{winter}}} = \sqrt{\frac{j(\text{O}^1\text{D})_{\text{summer}} \cdot [\text{O}_3]_{\text{summer}} \cdot [\text{H}_2\text{O}]_{\text{summer}}}{j(\text{O}^1\text{D})_{\text{winter}} \cdot [\text{O}_3]_{\text{winter}} \cdot [\text{H}_2\text{O}]_{\text{winter}}}} * \sqrt{\frac{k'_{\text{winter}}}{k'_{\text{summer}}}} \quad (5.11)$$

assuming that the other factors that make up f are approximately constant between the seasons. Table 5.2 shows the midday hour (12:00-13:00 Australian Eastern Standard Time (AEST)) and daytime (06:00-19:00 AEST) mean values of each quantity in Equation (5.11) for both summer and winter campaigns (except k' ; see below).

Table 5.2 *Midday (12:00-13:00 AEST) and daytime (06:00-19:00 AEST) mean values of selected quantities during SOAPEX 1a, 1b and the equivalent 1a/1b ratios*

Campaign	Time	$[\text{HO}_2 + \text{RO}_2]$ /pptv	$j(\text{O}^1\text{D})$ / $\times 10^{-5} \text{ s}^{-1}$	$[\text{O}_3]$ /ppbv	$[\text{H}_2\text{O}] / \times 10^{17}$ molecules cm^{-3}
SOAPEX 1a	Midday	10.8	2.6	17.0	3.1
(summer)	Daytime	6.6	1.2	16.4	3.1
SOAPEX 1b	Midday	6.7	0.9	31.6	2.6
(winter)	Daytime	3.3	0.3	31.3	2.6
1a/1b ratio	Midday	1.6	3.0	0.5	1.2
	Daytime	2.0	4.3	0.5	1.2

The ratio of the peak (midday) measured peroxy radical levels for SOAPEX 1a/ SOAPEX 1b was 1.6. The ratio of summer/winter maximum $j(\text{O}^1\text{D})$ levels was 3.0, the summer/winter midday ratio of $[\text{H}_2\text{O}]$ was 1.2, and the equivalent summer/winter ozone ratio was 0.5. Assuming initially that k' was invariant with season, Equation (5.11) gave a summer/winter ratio for $[\text{HO}_2 + \text{RO}_2]$ of 1.4, which is in moderate agreement with the measured value (1.6). A

similar level of agreement was obtained using the daytime averaged data (1a/1b $[\text{HO}_2 + \text{RO}_2]$ ratio 2.0; 1a/1b $\sqrt{j(\text{O}^1\text{D}) \cdot [\text{O}_3] \cdot [\text{H}_2\text{O}]}$ ratio 1.6).

Modelling by Dr Greg Ayers (CSIRO, Australia) of the MBL conditions found at Cape Grim (based on the model published by Ayers *et al.* [1997a]) suggested, however, that the $\text{HO}_2/\text{CH}_3\text{O}_2$ ratio (β in Equation 5.10) varied appreciably with season (as noted for Mace Head in Section 4.4), from 0.6 in summer to 0.8 in winter, leading to a calculated ratio of $k'_{\text{winter}}/k'_{\text{summer}}$ of 1.2. Using the modelled ratio of k' in Equation (5.11) enabled a revised midday $[\text{HO}_2 + \text{RO}_2]$ summer/winter ratio of $1.4 \cdot \sqrt{1.2} = 1.5$ to be calculated, which is in closer agreement with the experimental result (1.6). Similar results were obtained from the daytime averaged data (1a/1b measured $[\text{HO}_2 + \text{RO}_2]$ ratio 2.0; calculated $[\text{HO}_2 + \text{RO}_2]$ ratio 1.8). These results demonstrate that Equation (5.5) is a good description of the behaviour of peroxy radicals in the remote, low- NO_x MBL. In addition, since the midday ratio of $\sqrt{j(\text{O}^1\text{D})}$ summer/winter was 1.7, it may be concluded that the reduction in ozone photolysis in the winter months was the primary factor responsible for the lower peroxy radical levels observed in winter compared with summer during the SOAPEX 1 campaigns. That there was approximately twice the mixing ratio of ozone present in winter meant, however, that the radical levels did not fall as markedly as would be expected from consideration of the $j(\text{O}^1\text{D})$ values in isolation.

5.1.4 PERCA underestimation of peroxy radical mixing ratios during SOAPEX 1

Monks *et al.* [1998] showed by two independent methods that the PERCA instrument underestimated peroxy radical mixing ratios during SOAPEX 1a by a factor of about 2. The first method compared estimates of k' (see Section 5.1.3) for each day of baseline conditions based on measured peroxy radicals and Equation (5.5), with theoretical values of k' , based on calculated rate coefficients for the conditions encountered and various possible values of β (0.25-3.0). The theoretical k' values lay in the range $(0.9-5.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, whereas the 'measured' values lay in the range $(0.9-1.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For an assumed β value of 1.0 ($[\text{HO}_2] = [\text{CH}_3\text{O}_2]$), the mean discrepancy in the derived values of k' was a factor of 4.8 (measured/theoretical), which implied (from Equation 5.5) an underestimation by the PERCA instrument of a factor of 2.2. Very similar results were obtained using the same analysis for the winter campaign (SOAPEX 1b): this was taken as evidence that the underestimation by the PERCA was similar for both campaigns, and

allowed calculation of the ratios presented in the last section to be made without adding the complication of the PERCA humidity effect to the problem [Monks *et al.*, 2000].

The second analysis method utilised the fact that peroxy radical self- and cross-reactions represent by far the most important source of gas-phase peroxides in the troposphere. By writing hydrogen peroxide (H_2O_2) and total organic peroxide (ROOH) continuity equations, it is possible to calculate theoretical peroxy radical mixing ratios from consideration of measured peroxide mixing ratios. This method is discussed further in Section 5.2, where the same approach is adopted for the SOAPEX 2 campaign. For averaged baseline conditions during SOAPEX 1a, the peroxide calculations yielded a theoretical midday maximum $[\text{HO}_2 + \text{RO}_2]$ of 17.4 pptv. The measured midday maximum $[\text{HO}_2 + \text{RO}_2]$ value was 10.1 pptv, implying a discrepancy in the PERCA measurements of a factor of 1.7.

5.2 The SOAPEX 2 Campaign

5.2.1 Objectives of the Experiment

The main objectives of the second SOAPEX field campaign in 1999 may be summarised as follows:[†]

- (1) In the light of the SOAPEX 1 results, to test further fast photochemical theory in clean air – in particular to examine the relationships between $j(\text{O}^1\text{D})$, OH and peroxy radicals using not only PERCA $[\text{HO}_2 + \text{RO}_2]$ measurements, but also University of Leeds FAGE OH and HO_2 measurements (see Chapter 1 for a brief introduction to this measurement technique).
- (2) To examine perturbations from the baseline case in more polluted air masses arriving at CGBAPS from continental Australia.
- (3) To investigate the balance between photochemical ozone production and destruction under different pollution regimes.
- (4) To test instrumental performance: as indicated in Section 5.1, the PERCA instrument was found to underestimate peroxy radical mixing ratios in SOAPEX 1 by a factor of about 2. It was expected that in SOAPEX 2, with the much fuller range of measurements undertaken, including independent (FAGE) HO_2 measurements, and high-quality volatile organic compound (VOC) and NO_x/NO_y measurements, the

[†] This material is adapted from the original SOAPEX 2 research proposal to the NERC.

discrepancy could be better quantified, possibly even removed. The effect of maintaining the inlet of the PERCA instrument at 30 °C (as for EASE 96 and 97 – see Chapter 4) could be examined, especially in the light of the laboratory characterisation experiments of the instrument also undertaken in the present project (Chapter 2). Of course, field testing and development of a number of other instruments was also an important part of the SOAPEX project, albeit not covered in this thesis.

- (5) To test model representations of tropospheric chemistry, in particular boundary layer processes: mixing between the free troposphere and the boundary layer, deposition processes, etc.

5.2.2 Measurements and instrument operators during SOAPEX 2

A summary of measurements undertaken during SOAPEX 2, together with the organisations responsible, is given in Table 5.3. In addition, the suite of measurements carried out routinely at CGBAPS by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Atmospheric Research Division were also available for the SOAPEX campaign period, including CO, CH₄, meteorological parameters, CN particle measurements, CFCs and aerosols [*Baseline Atmospheric Program, Australia, 1976-1996*].

5.3 The PERCA Measurements during SOAPEX 2

5.3.1 Instrument operation

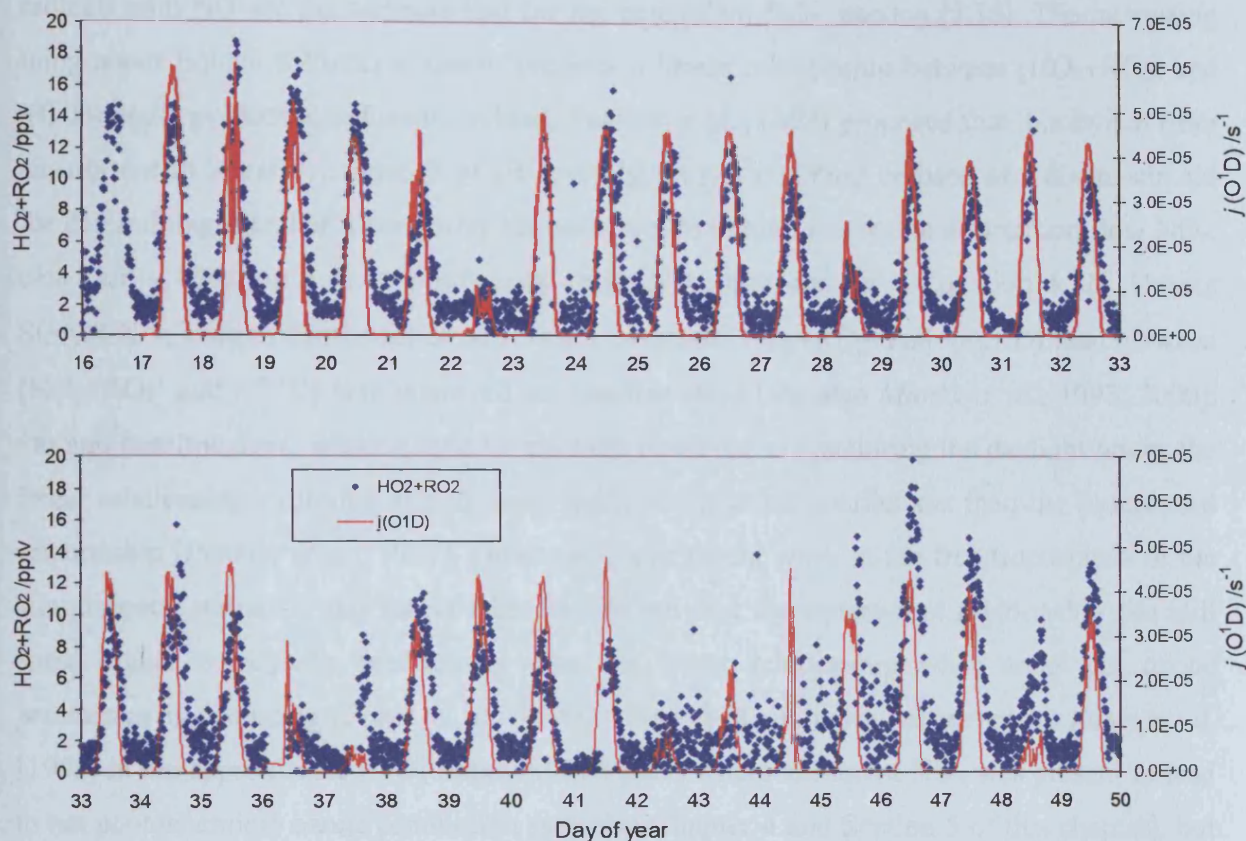
During SOAPEX 2, the PERCA instrument ran virtually continuously from 16th January – 18th February inclusive (days of year 16-49). The only days with substantial measurement periods lost were as follows: day 23 (failure of luminol solution); day 36 (power cut); days 43-45 (repairs and calibrations). In addition, regular calibrations were performed every 5-7 days during the campaign. The PERCA chain length (CLN) during the campaign (see Chapters 1 and 2) was relatively low, but stable (mean value 48, standard deviation 4.5). The entire peroxy radical data set obtained with the PERCA instrument during SOAPEX 2 is shown in Figure 5.2 (10 min averages); concomitant $j(\text{O}^1\text{D})$ measurements are also shown in Fig. 5.2 as a visual aid. Fig. 5.2 shows that the maximum in peroxy radical mixing ratios generally coincided with the maximum in $j(\text{O}^1\text{D})$, as predicted by simple photochemical theory, and seen previously in a number of field campaigns, including SOAPEX 1 and the EASE experiments at Mace Head (Chapter 4). The obvious exceptions to the rule were during the night-time periods 43-44 and 44-45, where relatively high spikes in the mixing ratios of

peroxy radicals were observed. These spikes were probably not representative of the true night-time peroxy radical levels on those nights, however, and disappeared on averaging the data up to half-hourly/hourly means. It is also worth noting that the relative magnitude of the midday peak in peroxy radicals from day to day often corresponded well with the relative value of the maximum in $j(\text{O}^1\text{D})$, for example days 18-21 and days 45-49, although exceptions can also be found (*cf.* days 39-41).

Table 5.3 *Measurements undertaken during SOAPEX 2*

Species/Quantity	Technique	Organisation ^a
OH	FAGE	1
Peroxy radicals	FAGE [HO_2], PERCA [$\text{HO}_2 + \text{RO}_2$]	1, 2
Photolysis frequencies including $j(\text{O}^1\text{D})$ and $j(\text{NO}_2)$	Filter and spectral radiometry	1, 2, 4
O_3	UV (Thermoelectron Model 49 ozone monitor)	1, 4
NO	Custom-built NO/ O_3 chemiluminescence detection system	3, 4
NO_2	As above, with photochemical $\text{NO}_2 \rightarrow \text{NO}$ conversion	3, 4
NO_y	As above, with gold tube/ CO $\text{NO}_y \rightarrow \text{NO}$ conversion	3, 4
HOOH, ROOH	Dual-channel fluorimetric detector	4
HCHO	Fluorimetric detector based upon Hantzsch reaction	4
VOCs, including DMS, HCHO	High-frequency automated GC	1
Nitrate radical, NO_3 (also IO)	DOAS (Differential Optical Absorption Spectroscopy)	3
Short-lived halocarbons	GC	3
Alkyl nitrates, peroxy acetyl nitrate (PAN)	GC	3

^a 1 University of Leeds, UK; 2 University of Leicester, UK; 3 University of East Anglia, UK; 4 CSIRO, Australia (see text for details).

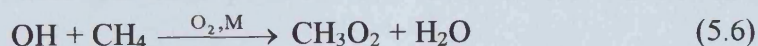
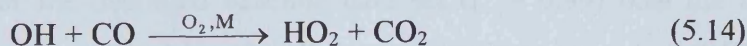
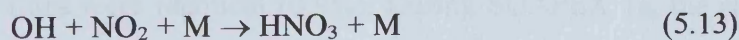
Figure 5.2 PERCA and $j(O^1D)$ data during SOAPEX 2 (10 min averages)

5.3.2 Correlations of $[HO_2+RO_2]$ with $j(O^1D)$

As discussed in Section 5.1.3, in clean, low- NO_x air, Penkett *et al.* [1997] showed that $[HO_2+RO_2]$ is proportional to $\sqrt{j(O^1D)}$ (Equation 5.5). In contrast, in more polluted air, where the peroxy radical losses are dominated by their reactions with NO , and HO_x ($OH + HO_2$) is predominantly lost via the reaction of OH with NO_2 (reaction 5.13), a different relationship was suggested [see also Chapter 4; Penkett *et al.*, 1997]:

$$[HO_2 + RO_2] = \frac{2f \cdot j(O^1D)[O_3]}{k_{13}[NO_2]} \left(\frac{k_{14}[CO] + k_6[CH_4]}{k_{15}[NO]} \right) \quad (5.12)$$

where f is defined as for Equation (5.5), and k_i is the rate coefficient for the reaction (5.i):



Equation (5.12) assumes that the rate coefficients for the reactions of the organic peroxy radicals with NO are the same as that for the equivalent HO_2 reaction (5.15). The interesting thing about Equation (5.12) is that it predicts a *linear* relationship between $[\text{HO}_2 + \text{RO}_2]$ and $j(\text{O}^1\text{D})$ under polluted conditions. Indeed, *Penkett et al.* [1997] proposed that this switch from square-root to linear dependence of $[\text{HO}_2 + \text{RO}_2]$ on $j(\text{O}^1\text{D})$ could be used as a diagnostic aid for determining whether a particular air mass would exhibit net ozone destruction (low NO_x , clean air – Equation 5.5) or production (high NO_x , polluted air – Equation 5.11). During SOAPEX 1, a significantly better correlation between $[\text{HO}_2 + \text{RO}_2]$ and $\sqrt{j(\text{O}^1\text{D})}$ than between $[\text{HO}_2 + \text{RO}_2]$ and $j(\text{O}^1\text{D})$ was observed on baseline days [see also *Monks et al.*, 1998, 2000]. On non-baseline days, where ozone levels were observed to rise during the daylight hours, the linear relationship exhibited significantly higher correlation coefficients than the square-root relationship [*Penkett et al.*, 1997]. However, more recent work in the free troposphere at the Jungfraujoch station in the Swiss Alps has shown that the square-root relationship can still show higher correlation coefficients than the linear relationship when small net ozone production is occurring [*Zanis et al.*, 1999]. Such behaviour was observed by *Zanis et al.* [1999] in the approximate $[\text{NO}]$ range 20-100 pptv, where sufficient NO_x was present to lead to net photochemical ozone production (see also Chapter 4 and Section 5 of this chapter), but where the main peroxy radical termination processes were still the peroxy radical self- and cross-reactions to give peroxides and other non-radical products (reactions 5.7-5.9).

Figure 5.3 shows a scatter plot of the correlation coefficients (r^2 values) obtained from the square root relationship (abscissa) between $[\text{HO}_2 + \text{RO}_2]$ and $j(\text{O}^1\text{D})$ *versus* those obtained from the linear relationship (ordinate) for each day during SOAPEX 2 where data were available. In each case, the correlation coefficients were derived from plots using data between the hours 06:00 and 14:00 (hourly averages) only, as the dependence of peroxy radical levels on actinic flux generally weakens in the afternoon, whether clean or polluted conditions are encountered [*Monks et al.*, 1996, 1998]; this point is discussed further in Chapter 3. Fig. 5.3 shows that there was generally very little difference between the degrees of correlation of $[\text{HO}_2 + \text{RO}_2]$ *versus* $j(\text{O}^1\text{D})$ and $[\text{HO}_2 + \text{RO}_2]$ *versus* $\sqrt{j(\text{O}^1\text{D})}$ during SOAPEX 2. Although the linear correlation was on average slightly higher (LIN mean $r^2 = 0.86$; SQRT mean $r^2 = 0.85$), the median values were identical (0.95₅). During SOAPEX 1a, the square root correlation was higher for the averaged baseline data set ($r^2 = 0.99$) than the linear correlation ($r^2 = 0.97$); for the averaged 'semi-polluted' data set the reverse was true (SQRT $r^2 = 0.90$, LIN $r^2 = 0.96$).

Perhaps more revealing is a consideration of the relationship between the ratio ($\text{LIN } r^2/\text{SQRT } r^2$) and net photochemical ozone tendency ($\text{N}(\text{O}_3)$), defined as in Chapter 4 (Figure 5.4; see Section 5.5 for discussion of the ozone tendencies observed during SOAPEX 2). Fig. 5.4 shows that there was no significant correlation between the ratio ($\text{LIN } r^2/\text{SQRT } r^2$) and $\text{N}(\text{O}_3)$ during SOAPEX 2, *i.e.*, the extent of correlation of $[\text{HO}_2+\text{RO}_2]$ versus $j(\text{O}^1\text{D})$ and $[\text{HO}_2+\text{RO}_2]$ versus $\sqrt{j(\text{O}^1\text{D})}$ could not be used as a criterion for predicting net ozone production/destruction for the conditions encountered. Inspection of individual days during SOAPEX 2 showed that the 'LIN or SQRT best correlation' criterion successfully predicted net ozone destruction/production on only 13 of 30 days during the campaign where all necessary data were available for analysis.

Figure 5.3 Scatter plot of the correlation coefficients (r^2 values) obtained from the square root relationship (abscissa) between $[\text{HO}_2+\text{RO}_2]$ and $j(\text{O}^1\text{D})$ versus those obtained from the linear relationship (ordinate)

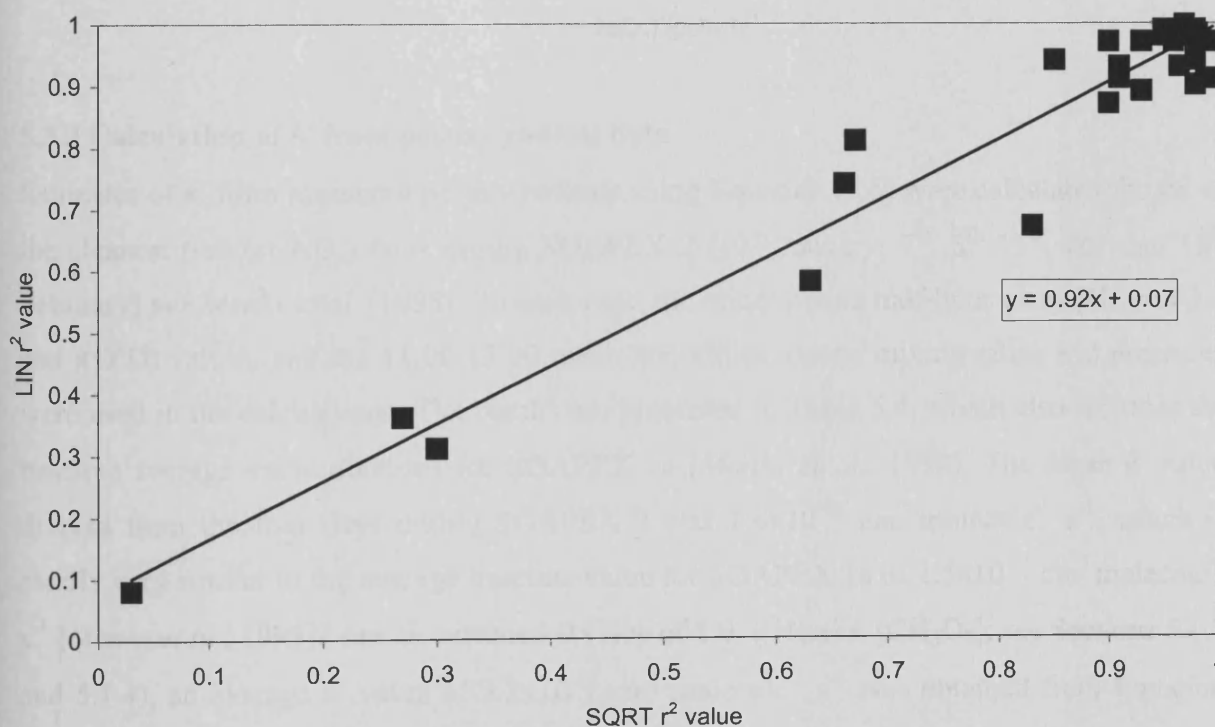
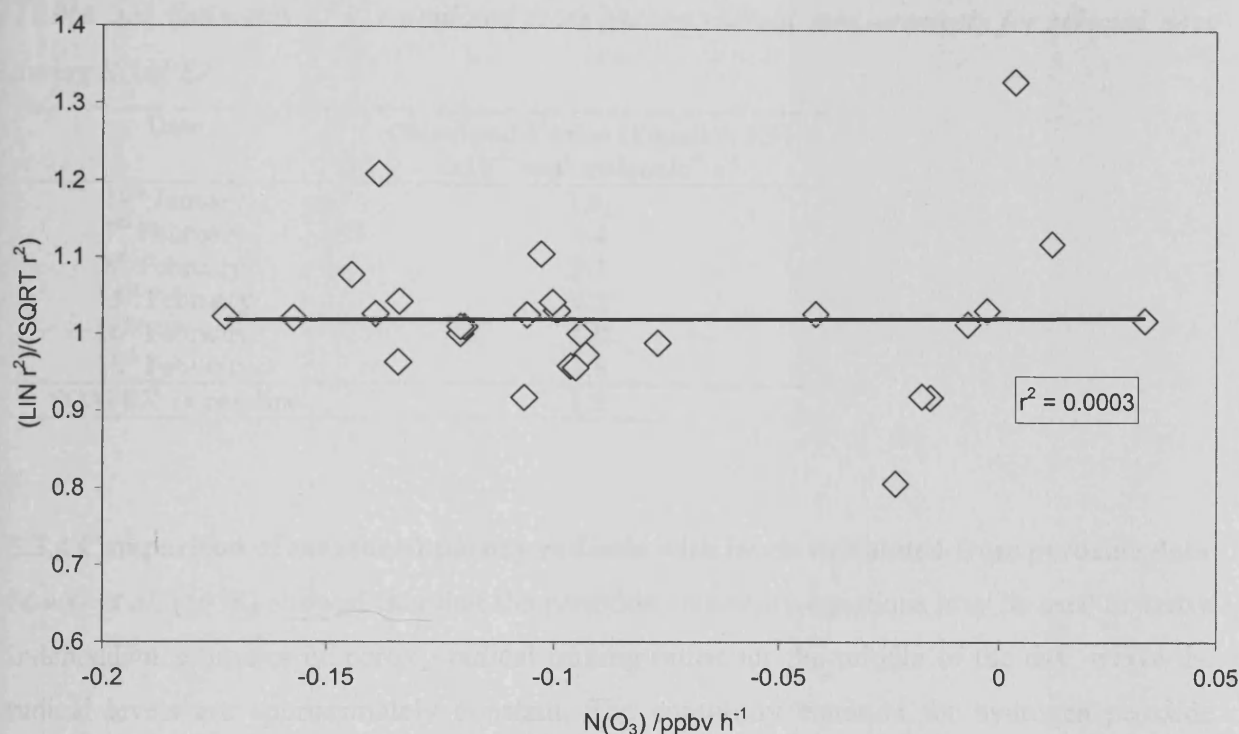


Figure 5.4 The relationship between the ratio of the correlation coefficients (r^2 values) obtained from the square root and linear correlations of $[HO_2+RO_2]$ and $j(O^1D)$ and ozone tendency ($N(O_3)$) for each day during SOAPEX 2



5.3.3 Calculation of k' from peroxy radical data

Estimates of k' from measured peroxy radicals using Equation (5.5) were calculated for six of the cleanest (lowest NO_x) days during SOAPEX 2 (19th January; 7th, 8th, 15th, 16th and 18th February) *per Monks et al.* [1998]. In each case, the midday peak half-hour mean $[HO_2+RO_2]$ and $j(O^1D)$ values, and the 11:00-13:00 mean humidities, ozone mixing ratios and pressures were used in the calculations. The results are presented in Table 5.4, which also includes the baseline average value obtained for SOAPEX 1a [*Monks et al.*, 1998]. The mean k' value derived from the four days during SOAPEX 2 was $1.6 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, which is clearly very similar to the average baseline value for SOAPEX 1a of $1.5 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ [*Monks et al.*, 1998]. For an assumed β value of 1.0 ($[HO_2] = [CH_3O_2]$; see Sections 5.1.3 and 5.1.4), an average k' value of $3.2 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ was obtained from Equation (5.10)[†]: a factor of 5.0 smaller than the mean value estimated from the peroxy radical measurements ($1.6 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$). Because of the square root relationship between $[HO_2+RO_2]$ and k' (Equation 5.5), this result implies that the PERCA instrument measured a

[†] The calculated k' value was in the range $2\text{--}4 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, depending on an assumed HO_2/RO_2 ratio in the range 0.5-2 [*cf. Monks et al.*, 1998].

factor of $ca \sqrt{5.0} = 2.2$ low during SOAPEX 2; the analogous result from SOAPEX 1a was also 2.2 [Monks *et al.*, 1998].

Table 5.4 Estimates of k' calculated from peroxy radical measurements for selected days during SOAPEX 2

Date	Calculated k' value (Equation 5.5) / $\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
19 th January	1.0 ₅
7 th February	1.4
8 th February	2.3
15 th February	1.2
16 th February	1.9
18 th February	1.9
SOAPEX 1a baseline	1.5

5.3.4 Comparison of measured peroxy radicals with levels calculated from peroxide data

Monks *et al.* [1998] showed that the peroxide continuity equations may be used to derive independent estimates of peroxy radical mixing ratios for the middle of the day, where the radical levels are approximately constant. The continuity equation for hydrogen peroxide (H_2O_2) may accordingly be written as follows (*cf.* Equation 5.4, the equivalent expression for ozone):

$$\frac{\Delta \text{H}_2\text{O}_2}{\Delta t} = k_7 [\text{HO}_2]^2 - \left(\frac{v_d}{H} \right) [\text{H}_2\text{O}_2] - j_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] \quad (5.16)$$

where k_7 is the rate coefficient for the HO_2 self-reaction (5.7), v_d is the dry deposition velocity of H_2O_2 (0.01 m s^{-1}), H is the boundary layer height (1000 m) [Ayers *et al.*, 1996], and $j_{\text{H}_2\text{O}_2}$ is the photolysis rate of H_2O_2 , which is also approximately constant in the middle of the day. Rearrangement of Equation (5.16) gives:

$$[\text{HO}_2] = \left\{ \left(\frac{\Delta \text{H}_2\text{O}_2}{\Delta t} + \left(\frac{v_d}{H} \right) [\text{H}_2\text{O}_2] + j_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] \right) / k_7 \right\}^{1/2} \quad (5.17)$$

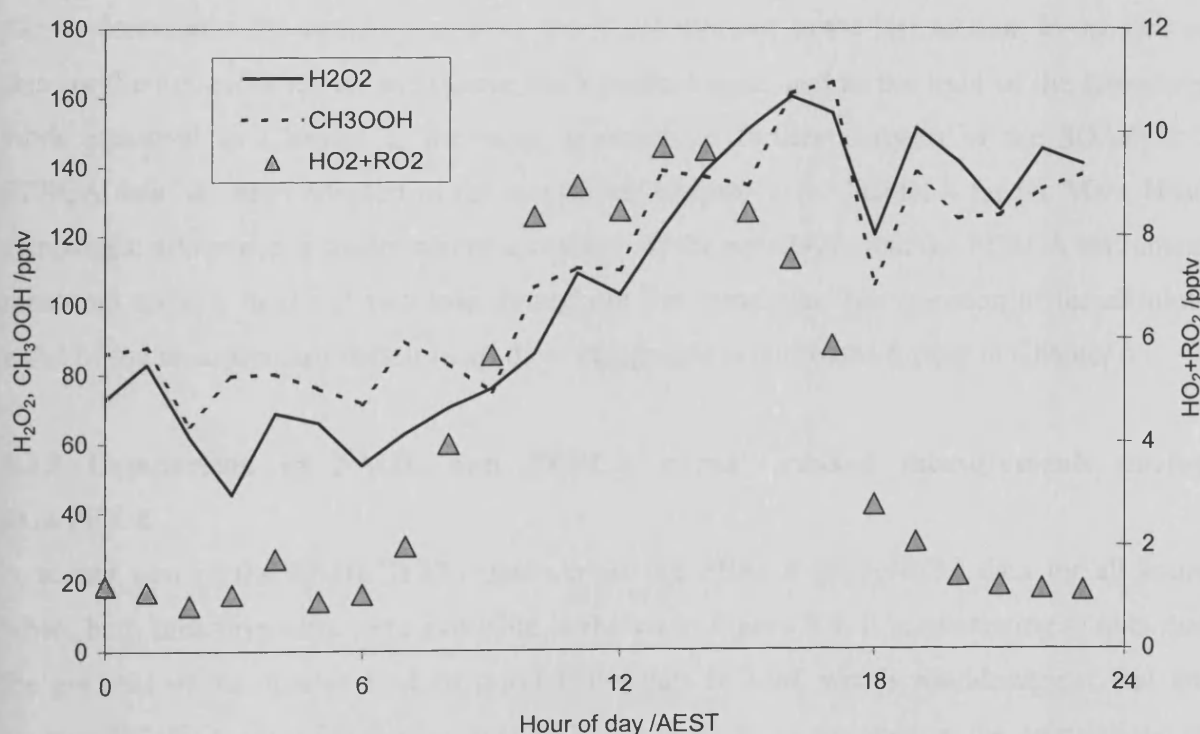
Given an estimate for $[\text{HO}_2]$, the analogous continuity equation for CH_3OOH can be rearranged to give an estimate of $[\text{CH}_3\text{O}_2]$:

$$[\text{CH}_3\text{O}_2] = \frac{\left(\frac{\Delta\text{CH}_3\text{OOH}}{\Delta t} + \left(\frac{v_d}{H} \right) [\text{CH}_3\text{OOH}] + j_{\text{CH}_3\text{OOH}} [\text{CH}_3\text{OOH}] \right)}{k_9 [\text{HO}_2]} \quad (5.18)$$

where k_9 is the rate coefficient for the $\text{HO}_2 + \text{CH}_3\text{O}_2$ reaction (5.9), and assuming in this analysis that CH_3OOH makes up the entire ROOH signal (Table 5.3), which is likely to be a reasonable assumption under clean-air conditions [Monks *et al.*, 1998].

Figure 5.5 shows hourly-averaged peroxide and peroxy radical data for 7th February 1999, which was one of the cleanest (lowest NO_x) days encountered during the campaign. The steady build-up of both H_2O_2 and CH_3OOH during daylight hours is clearly shown in Fig.5.5, as are the relatively minor changes in peroxy radical mixing ratios (range 8.5-9.7 pptv) during the middle of the day (11:00-13:00 AEST).

Figure 5.5 SOAPEX 2 Day 38 (7th February 1999) hourly averaged hydrogen peroxide, methyl hydrogen peroxide and peroxy radical data



Midday peroxy radical mixing ratios were calculated from peroxide data (Equations 5.17 and 5.18) for six of the cleanest days observed during SOAPEX 2 (19th January; 7th, 8th, 15th, 16th and 18th February) by calculating mean daytime $\{\Delta(\text{peroxide})/\Delta t\}$ values from plots such as

Fig. 5.5; the midday peroxide photolysis rates were calculated for each day using the procedure described in Section 5.6. The results of this analysis are presented in Table 5.5.

Table 5.5 *Calculated midday peroxy radical mixing ratios for selected days during SOAPEX 2*

Day	Midday [H ₂ O ₂] /pptv	$\Delta(\text{H}_2\text{O}_2)$ / Δt /pptv h ⁻¹	Midday [CH ₃ OOH] /pptv	$\Delta(\text{CH}_3\text{OOH})$ / Δt /pptv h ⁻¹	Calc. [HO ₂] /pptv	Calc. [CH ₃ O ₂] /pptv	Calc. [HO ₂ + CH ₃ O ₂] /pptv	Meas. [HO ₂ + CH ₃ O ₂] /pptv	Calc. /Meas. ratio
19 th Jan	254	9.7	293	8.5	6.9	6.3	13.2	14.5	0.91
7 th Feb	103	10.9	110	8.4	5.6	4.5	10.1	9.7	1.04
8 th Feb	147	12.4	239	20.0	6.2	9.3	15.5	7.9	1.96
15 th Feb	263	1.5	148	4.1	5.7	3.7	9.4	17.0	0.55
16 th Feb	163	3.2	a	a	4.9	a	9.4 ^a	11.4	0.82
18 th Feb	126	9.1	a	a	5.5	a	10.6 ^a	11.4	0.93

^a No reliable CH₃OOH data were available for 16th, 18th Feb; in order to estimate [CH₃O₂] for these days, the mean calculated HO₂/CH₃O₂ ratio for the other days was used.

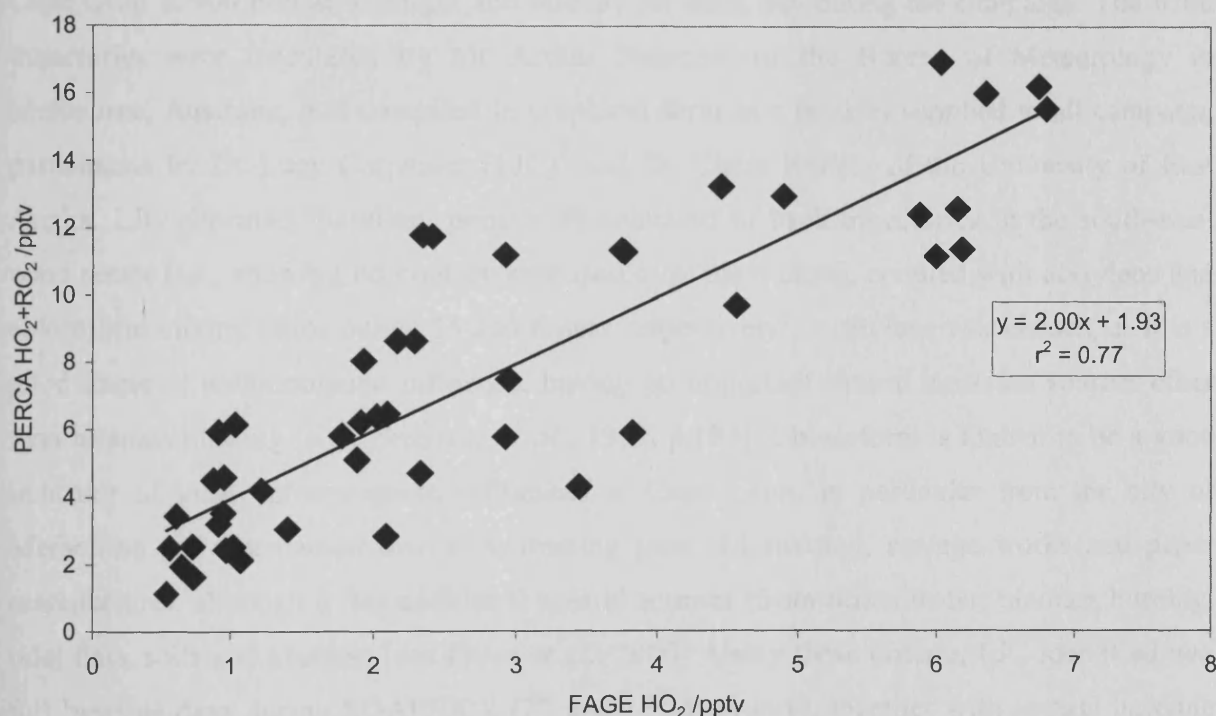
Table 5.5 shows that the midday maximum calculated and measured peroxy radical mixing ratios were fairly similar for four of the six days; the average calculated/measured ratio over all six days was 1.0 (1.1 if 16th and 18th February were excluded). This ratio implies that the PERCA instrument measured only marginally low, if at all, during the campaign, which clearly contradicts the conclusions from the k' calculations in the last section. In the face of this conflicting evidence on the instrument's performance, and in the light of the laboratory work presented in Chapter 2, the same approach to further analyses of the SOAPEX 2 PERCA data has been adopted in the rest of this chapter as in Chapter 4 for the Mace Head campaigns: allowance is made, where necessary, of the possibility that the PERCA instrument measured up to a factor of two low throughout the campaign. The question of the absolute value of the measurement deficit in all three campaigns is addressed further in Chapter 6.

5.3.5 Comparison of FAGE and PERCA peroxy radical measurements during SOAPEX 2

A scatter plot of the FAGE [HO₂] data *versus* the PERCA [HO₂+RO₂] data for all hours where both measurements were available is shown in Figure 5.6. It is interesting to note that the gradient of the line of best fit through the data is 2.00, which would suggest that the average HO₂/RO₂ ratio (β) during SOAPEX 2 was *ca* 1, as assumed in the calculations of Section 5.3.3. When the non-zero intercept of the plot was considered, however, the mean HO₂/RO₂ ratio was calculated to be 0.59 (median 0.51), which is in very good agreement with the modelled value for Cape Grim summer baseline conditions of 0.61 [Ayers *et al.*, 1997; Monks *et al.*, 1998]. Nevertheless, it is worth noting that the data in Fig. 5.6 (taken

during the period 9th-16th February) are not all necessarily representative of baseline conditions (see Section 5.4); in addition, the estimated systematic errors in both sets of radical measurements are of the order 25-35% (Chapter 2), so that the calculated HO₂/RO₂ ratios are subject to an error of at least this magnitude. When the same calculation was made using

Figure 5.6 Scatter plot of the FAGE HO₂ data versus the PERCA [HO₂+RO₂] data for all hours where both measurements were available during SOAPEX 2



the radical measurements from 15th-16th February only (daytime periods identified as 'baseline' according to the criteria developed by Dr Lucy Carpenter of the University of East Anglia; see Section 5.4.1), the mean HO₂/RO₂ ratio was found to be 0.69. It is also worth noting that from the peroxide calculations of Section 5.3.4, the mean HO₂/RO₂ ratio from four very low-NO_x days during the campaign (19th January; 7th, 8th and 15th February; Table 5.4) was estimated to be 1.2. (The analogous result, based on three baseline days from SOAPEX 1a, was 1.5.) In conclusion, it would seem difficult to judge whether the measured HO₂/RO₂ ratio was really representative of conditions experienced at Cape Grim during SOAPEX 2: in view of the likely underestimation of peroxy radical mixing ratios by the PERCA instrument, the good agreement with modelled results is not readily explicable.

5.4 Classification of Air Masses during SOAPEX 2

5.4.1 Introduction to the classification methods

Very few periods of baseline conditions using the CSIRO criteria of wind sector coupled with CN counts of fewer than 600 cm^{-3} were observed during SOAPEX 2. For this reason, four alternative methods for classifying air masses during SOAPEX 2 were investigated during the course of this work. The first method relied on the use of 5-day back trajectories ending at Cape Grim at 900 hPa at midnight and midday for each day during the campaign. The wind trajectories were calculated by Mr Arthur Downey, of the Bureau of Meteorology in Melbourne, Australia, and compiled in graphical form in a booklet supplied to all campaign participants by Dr Lucy Carpenter (LJC)[†] and Dr Claire Reeves of the University of East Anglia. LJC allocated 'baseline' periods by selection of back-trajectories in the south-west wind sector (*i.e.*, showing no contact with land over the 5 days), coupled with acetylene and chloroform mixing ratios below 15 and 6 pptv respectively[‡]. Acetylene was chosen, as it is a good tracer of anthropogenic influence, having no important natural emission sources other than biomass burning [*e.g.*, Brasseur *et al.*, 1999, p.184]. Chloroform is known to be a good indicator of local anthropogenic influences at Cape Grim, in particular from the city of Melbourne and Tasmanian towns (swimming pool chlorination, sewage works and paper manufacture), although it has additional natural sources (from ocean water, biomass burning, tidal flats, soils and grasses) [see Prinn *et al.*, 2000]. Using these criteria, LJC identified two full baseline days during SOAPEX 2 (7th and 18th February), together with several baseline daytime (19th-20th January, 15th-16th February) and night-time (19th-20th January; 6th-7th, 7th-8th, 15th-16th and 17th-18th February) periods. For the analyses presented in this chapter, 'baseline' and 'non-baseline' composite diel cycles were compiled for all measurements made during the campaign.

The second method used for air mass classification during SOAPEX 2 was based on the wind direction measured at Cape Grim, using only data where the recorded wind speed was greater than 3 m s^{-1} (*cf.* Chapter 4). Figure 5.7 shows that the distribution of wind directions recorded during SOAPEX 2 was bimodal, to a first approximation, with a definite minimum at about 150° ; the highest frequencies were observed virtually in the easterly direction ('semi-polluted'). There were very few data in the range $300\text{--}20^\circ$, so that data could be divided into

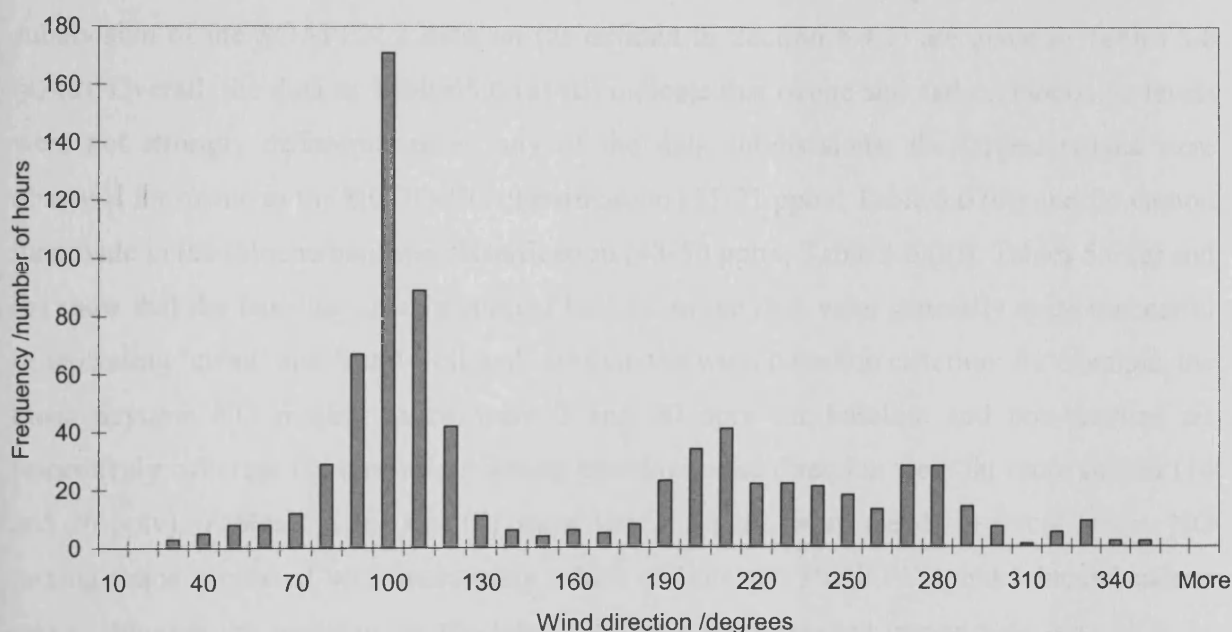
[†] Now at the University of York.

[‡] This alternative baseline selection method is assumed throughout the remainder of the chapter.

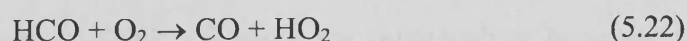
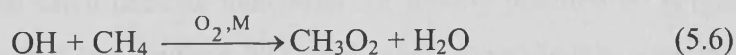
approximate 'clean' and 'semi-polluted' sectors using the simple cut-off point of 150°, where the 'clean' data were taken to be >150°.

The remaining air mass classification methods utilised pollution tracer ratios, in an effort to separate air masses of differing ages, *i.e.*, differing times since last major impact by pollution. The tracer ratios used were formaldehyde / carbon monoxide (HCHO/CO) and toluene

Figure 5.7 Frequency distribution of wind directions measured at Cape Grim during SOAPEX 2 (hourly averages)



/benzene. The HCHO/CO ratio is of potential interest since both tracers are not only primary pollutants [*e.g.*, Li *et al.*, 1997], but are also produced in the troposphere *via* the oxidation of methane in the presence of NO_x [*e.g.*, Wayne, 2000, pp. 331-2]:



The toluene/benzene ratio has been used in a number of previous studies to estimate air mass age, based on an estimated or measured emission ratio, coupled with knowledge of the

different rates of reaction of the two species with OH [*e.g.*, Lewis *et al.*, 1997], assuming that all other potential loss pathways /dispersion factors etc. are identical for both compounds.

The frequency distributions for both HCHO/CO and toluene/benzene (not shown) were unimodal during SOAPEX 2, with maxima at 0.0042 and 0.55, respectively. The data were therefore simply divided up into four bins for both tracers, where each bin was defined in order to contain 25% of the data set.

5.4.2 Results of the air mass classifications

Summaries of mean values of a number of chemical and climatological quantities for each subdivision of the SOAPEX 2 data set (as defined in Section 5.4.1) are given in Tables 5.6 (a)-(d). Overall, the data in Tables 5.6 (a)-(d) indicate that ozone and carbon monoxide levels were not strongly differentiated in any of the data subdivisions; the largest ranges were observed for ozone in the HCHO/CO classification (15-21 ppbv; Table 5.6 (c)) and for carbon monoxide in the toluene/benzene classification (43-50 ppbv; Table 5.6 (d)). Tables 5.6 (a) and (b) show that the baseline criteria applied by LJC to the data were generally more successful in separating 'clean' and 'semi-polluted' air than the wind direction criterion: for example, the mean daytime NO mixing ratios were 2 and 30 pptv for baseline and non-baseline air respectively, whereas the equivalent values based on wind direction were far more similar (14 and 20 pptv). Tables 5.6 (c) and (d) show less straightforward trends in tracer levels. NO mixing ratios increased with increasing values of both the HCHO/CO and toluene/benzene ratios, although the increase for the latter ratio was more marked (range 5-48 pptv NO). In contrast, the NO_x/NO_y ratio generally decreased with increasing HCHO/CO, which would suggest that higher values of the latter ratio are indicative of photochemically aged, 'semi-polluted' air; conversely, NO_x/NO_y increased with increasing toluene/benzene. This trend follows the established pattern in the literature, where relatively high NO_x/NO_y and toluene/benzene ratios are both often used as indicators for freshly polluted air (Figure 5.8). Nevertheless, it is noteworthy that the daytime NO (and other tracer) levels were low, even under 'semi-polluted' conditions, in comparison with the cleanest wind sectors observed at Mace Head during the EASE campaigns (see Chapter 4, Table 4.3, and Section 5.4.4).

The bottom three rows in each part of Table 5.6 show the relationships between various photochemically produced species and NO_z , the sum of the oxidation products of NO_x , for each tracer bin. The figures before the brackets are the mean ratios of the two quantities for a given data bin, whilst the figures in brackets are the gradients of the linear best-fit trend lines

Table 5.6 Summary of selected tracers for subdivisions of the SOAPEX 2 data set (see text for details)

(a) Trajectory analysis; acetylene, chloroform mixing ratios

Quantity	Baseline	Non-baseline
CO /ppbv	42	48
O ₃ /ppbv	17	17
NO /pptv ^a	2	30
NO _x /NO _y	0.15	0.45
Wind direction /°	240	131
HCHO/CO	0.0048	0.0053
Toluene/benzene	0.29	0.68
H ₂ O ₂ /NO _z ^b	0.95 (0.64)	0.77 (-0.01)
CH ₃ OOH/NO _z ^b	0.88 (0.57)	0.54 (0.01)
HCHO/NO _z ^b	1.13 (0.72)	0.93 (0.27)

(b) Wind direction

Quantity	>150° ('clean')	<150° ('semi-polluted')
CO /ppbv	45	49
O ₃ /ppbv	17	17
NO /pptv ^a	14	22
NO _x /NO _y	0.29	0.50
Wind direction /°	233	94
HCHO/CO	0.0050	0.0055
Toluene/benzene	0.52	0.70
H ₂ O ₂ /NO _z ^b	0.89 (0.34)	0.84 (0.08)
CH ₃ OOH/NO _z ^b	0.82 (0.03)	0.50 (0.06)
HCHO/NO _z ^b	1.04 (0.53)	1.09 (0.13)

(c) HCHO/CO ratio

Quantity	<0.0035	0.0035-0.005	0.005-0.007	>0.007
CO /ppbv	48	45	47	48
O ₃ /ppbv	15	16	18	21
NO /pptv ^a	13	18	24	29
NO _x /NO _y	0.66	0.59	0.41	0.45
Wind direction /°	154	165	164	148
HCHO/CO	0.002	0.004	0.006	0.009
Toluene/benzene	0.69	0.59	0.70	0.63
H ₂ O ₂ /NO _z ^b	1.79 (0.03)	1.38 (-0.26)	0.69 (0.07)	0.71 (-0.10)
CH ₃ OOH/NO _z ^b	1.62 (0.11)	1.02 (-0.21)	0.45 (0.10)	0.39 (0.03)
HCHO/NO _z ^b	1.09 (0.10)	1.57 (0.05)	1.10 (0.07)	1.37 (0.15)

^a Daytime mean. ^b Units pptv/pptv; figures in brackets are gradients of scatter plot linear trend lines (pptv/pptv).

Table 5.6 *cont.*

(d) Toluene/benzene ratio

Quantity	<0.4	0.4-0.55	0.55-0.7	>0.7
CO /ppbv	43	48	48	50
O ₃ /ppbv	17	18	17	17
NO /pptv ^a	5	19	33	48
NO _x /NO _y	0.24	0.38	0.48	0.47
Wind direction /°	211	137	124	115
HCHO/CO	0.005	0.006	0.006	0.005
Toluene/benzene	0.27	0.48	0.62	1.01
H ₂ O ₂ /NO _z ^b	0.85 (-0.02)	0.75 (0.05)	0.91 (-0.03)	0.58 (0.09)
CH ₃ OOH/NO _z ^b	0.61 (0.01)	0.51 (0.03)	0.54 (-0.01)	0.32 (0.06)
HCHO/NO _z ^b	1.30 (0.17)	1.00 (0.07)	1.25 (-0.14)	0.81 (-0.01)

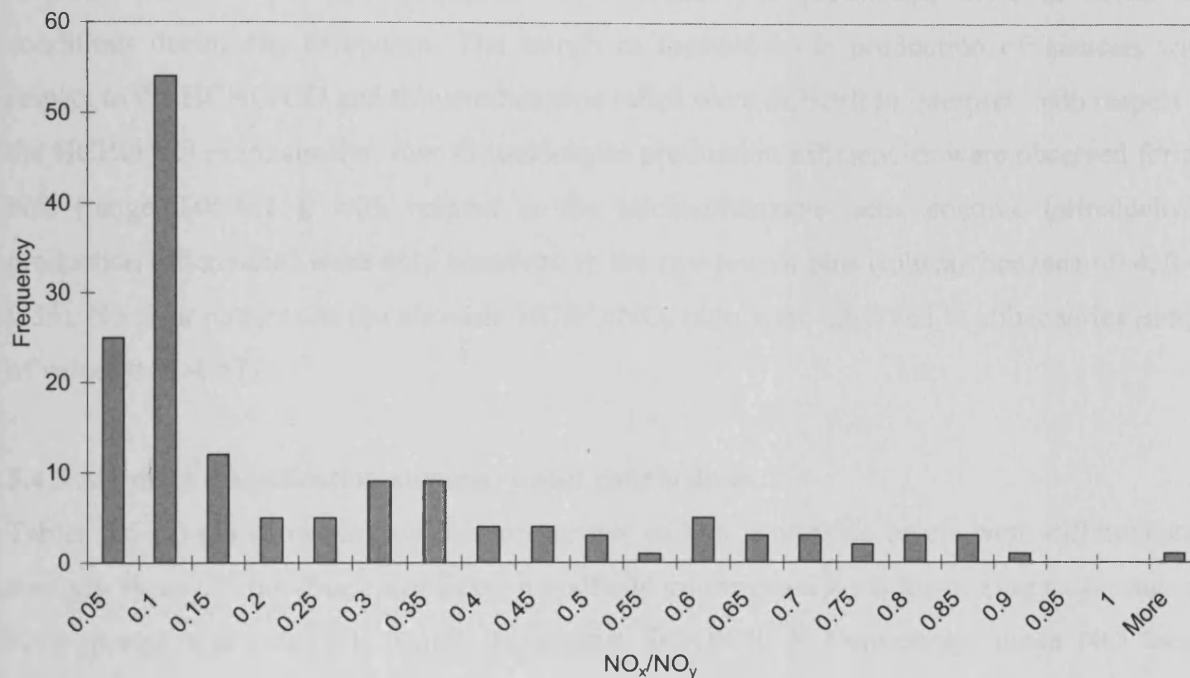
^a Daytime mean. ^b Units pptv/pptv; figures in brackets are gradients of scatter plot linear trend lines (pptv/pptv).

from scatter plots of the two quantities. These gradients have been used previously to estimate the production efficiency of peroxides, formaldehyde etc. with respect to NO_x oxidation, since for each compound C, they represent $\Delta C/\Delta \text{NO}_z$ (see also Chapter 4 and Section 5.5) [Li *et al.*, 1997].

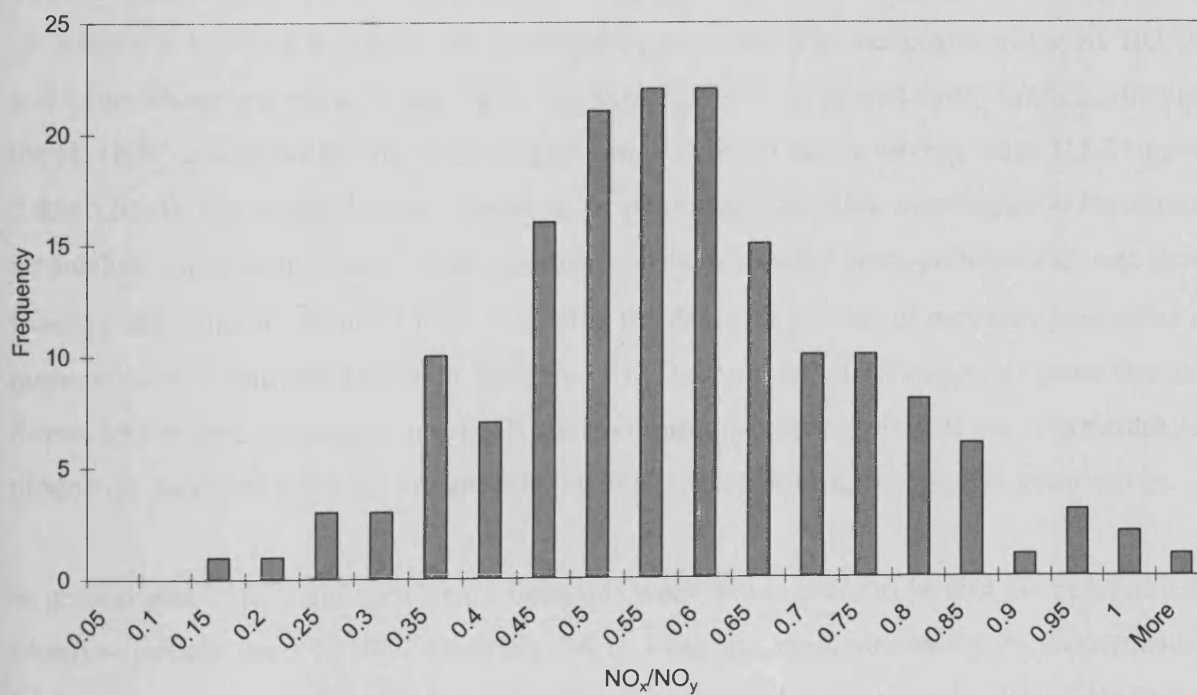
One might expect the relative production rate (and production efficiency) of the peroxides to decrease with increasing pollution levels (NO_x), as the peroxy radical self- and cross-reactions decrease in importance. Tables 5.6 (a) and (b) show once again that more marked differences could be observed between the baseline and non-baseline data sets than between the wind direction 'high' / 'low' data sets, both in the absolute ratios and in the production efficiencies. For example, the baseline production efficiency of CH₃OOH was 0.57, whereas the non-baseline value was negligibly small (0.01). Tables 5.6 (c) and (d) show that no clear trends were observed in the peroxide production efficiencies with increasing HCHO/CO or toluene/benzene: no values greater than 0.11 were observed in any of the data bins. However, the absolute ratios were generally observed to decrease with increasing HCHO/CO and toluene/benzene; this effect is more easily observed by consideration of the two extreme bins for each tracer ratio. For example, the H₂O₂/NO_z ratio was 1.79 for the lowest HCHO/CO bin (<0.0035) and 0.71 for the highest HCHO/CO bin (>0.007). This trend is indicative of higher absolute rates of peroxide production in the cleaner air masses (see also Section 5.5).

Figure 5.8 NO_x/NO_y frequency distributions for SOAPEX 2 data according to wind direction

(a) Wind direction $>150^\circ$



(b) Wind direction $<150^\circ$



Tables 5.6 (a) and (b) also show that there were markedly higher formaldehyde production efficiencies in 'clean' than in 'semi-polluted' air; in this case, the trend was obvious for both baseline and wind direction data selections. In contrast, the absolute HCHO/NO_z ratios were similar for all data bins, for example 1.04 for wind direction >150° and 1.09 for wind direction <150°, showing that significant formaldehyde production occurred across all conditions during the campaign. The trends in formaldehyde production efficiencies with respect to the HCHO/CO and toluene/benzene ratios were difficult to interpret: with respect to the HCHO/CO ratio, similar, low formaldehyde production efficiencies were observed for all bins (range 0.05-0.15); with respect to the toluene/benzene ratio, positive formaldehyde production efficiencies were only observed in the two lowest bins (toluene/benzene <0.4, 0.4-0.55). No clear patterns in the absolute HCHO/NO_z ratio were observed in either series (range of values 0.81-1.57).

5.4.3 Air mass classification summary and conclusions

Tables 5.6 (a)-(d) show that neither ozone nor carbon monoxide levels were differentiated strongly by any of the four classification methods investigated here; the mixing ratio range of both species was relatively small throughout SOAPEX 2. Conversely, mean NO levels generally were significantly different in each data subset, with the largest difference observed between baseline and non-baseline conditions (Table 5.6 (a)). Both the NO_x/NO_y and toluene/benzene ratios showed clear trends to higher values in non-baseline or 'semi-polluted' air relative to baseline or 'clean' air, as might be expected. The usefulness of the HCHO/CO and toluene/benzene ratios to segregate the SOAPEX 2 data proved fairly limited, although the HCHO/CO analysis provided the largest range of mean ozone mixing ratios (15-21 ppbv; Table 5.6 (c)). The mean absolute values of the peroxide/NO_z ratios were higher in the cleaner air subdivisions (baseline and wind direction >150°) than in the semi-polluted data sets (non-baseline and wind direction <150°), indicating the decrease in rates of peroxide production in more polluted conditions (see also Section 5.5). The production efficiency of peroxides and formaldehyde also decreased markedly in non-baseline (semi-polluted) air. Formaldehyde production appeared to be significant relative to NO_x oxidation across all data subdivisions.

In general terms, the main conclusion from this work would seem to be that the baseline data selection criteria used by LJC (Section 5.4.1) were the most successful in distinguishing 'clean' from 'semi-polluted' air masses during SOAPEX 2 [*cf. Lewis et al.*, 2001]. No further differentiation between air masses, for example showing local as opposed to Australian mainland pollution influences, could be achieved using the criteria examined here. As a

consequence, the baseline and 'semi-polluted' data divisions will be used to a large extent in data interpretation for the rest of this chapter.

5.4.4 Comparison of pollution tracer levels between SOAPEX 1a, SOAPEX 2 and the EASE campaigns

The range of species measured in SOAPEX 1 was more limited than in SOAPEX 2, but it is still useful to compare the conditions encountered in the two campaigns. Table 5.7 shows the mean values of a number of chemical tracers for SOAPEX 1a (summer) and SOAPEX 2 ('baseline' and 'semi-polluted', as defined for each campaign); also included in the table are the corresponding values for the EASE 96 and EASE 97 W and SE wind sectors. Table 5.7 shows that baseline conditions were more clearly differentiated from 'semi-polluted' conditions for all four tracers included during SOAPEX 1a than during SOAPEX 2. It is also evident from Table 5.7 that NO levels in 'semi-polluted' conditions at Cape Grim are generally as low as, if not lower than those in the cleanest conditions experienced at Mace Head (W wind sector); note also the substantially lower ozone, CO and CH₄ mixing ratios at the Southern Hemisphere site.

Table 5.7 Comparison of selected chemical tracers during SOAPEX 1a, SOAPEX 2, EASE 96 and EASE 97

Tracer	SOAPEX 1a		SOAPEX 2		EASE 96		EASE 97	
	Baseline ^a	'Semi-polluted' ^b	Baseline	'Semi-polluted'	W wind sector	SE wind sector	W wind sector	SE wind sector
NO	5	41	2	30	30	215	67	313
/pptv								
O ₃	16	18	17	17	30	36	34	38
/ppbv								
CO	44	60	42	49	98	128	151	165
/ppbv								
CH ₄	1666	-	1689	1694	1783	1828	1826	1852
/ppbv								

^a Monks *et al.* [1998]. ^b Carpenter *et al.* [1997].

Table 5.8 shows the H₂O₂/NO_z and HCHO/NO_z ratios for SOAPEX 2 (baseline and 'semi-polluted') together with the equivalent values for each wind sector from EASE 97, for comparison purposes. The data in Table 5.8 indicate that the hydrogen peroxide production efficiencies in the 'clean' sectors (NW, SW, W) during EASE 97 were significant (0.11-0.12), but much smaller than in baseline conditions during SOAPEX 2. The mixing ratios of peroxide relative to NO_z in the polluted SE sector at Mace Head in spring 1997 were much lower than the other sectors during the same campaign, and than at Cape Grim in austral

summer 1999. In contrast, the formaldehyde production efficiencies were relatively high across all air masses during EASE 97 (range 0.47-0.79), whilst the HCHO/NO_z absolute ratio was generally higher than for SOAPEX 2.

Table 5.8 SOAPEX 2 and EASE 97 hydrogen peroxide and formaldehyde production efficiencies

Campaign	Data set	H ₂ O ₂ /NO _z ^a	HCHO/NO _z ^a
SOAPEX 2	Baseline	0.95 (0.64)	1.13 (0.72)
	'Semi-polluted'	0.77 (-0.01)	0.93 (0.27)
	NW	1.18 (0.12)	1.96 (0.64)
EASE 97	NE	0.73 (-0.03)	1.39 (0.79)
	SE	0.23 (-0.09)	0.93 (0.47)
	SW	0.95 (0.11)	1.49 (0.41)
	W	0.76 (0.11)	1.26 (0.54)

^a Units pptv/pptv; figures in brackets are gradients of scatter plot linear trend lines (pptv/pptv).

5.5 Ozone Photochemistry during SOAPEX 2

5.5.1 Ozone tendencies

Daily (daytime) mean ozone tendencies (N(O₃)) were calculated for SOAPEX 2 by the two independent methods described in Chapter 4 for the EASE campaigns; first, using the measured peroxy radical mixing ratios to calculate the ozone production term:

$$N(O_3) = k_P[NO][HO_2 + RO_2] - \{f_j(O^1D) + k_2[OH] + k_3[HO_2]\}[O_3] \quad (5.23)$$

where k_P is a combined rate coefficient for the oxidation of NO to NO₂ by all peroxy radicals, and k_2 and k_3 are the rate coefficients for reactions (5.2) and (5.3) respectively.



Following the procedure described in Chapter 4 for EASE 96 and 97, N(O₃) calculations were carried out from Equation (5.23) both using the peroxy radical levels as measured, and the measured mixing ratios multiplied by two, to allow for the likely magnitude of the PERCA underestimation arising from the chain length-humidity effect (see Chapters 2 and 6). No

account was made in these calculations of the possible influence of halogen radical chemistry (see also Section 4.5), although recent observations at Cape Grim in mid-summer and mid-winter baseline conditions suggest the presence of an ozone destruction mechanism at sunrise, which cannot be accounted for by conventional HO_x chemistry [Galbally *et al.*, 2000]; similar observations have been reported from the north-west sub-tropical Pacific [Nagao *et al.*, 1999]. Indeed, during SOAPEX 2, measurements of iodine monoxide (IO) were obtained on 13 days (Table 5.3); some of these measurements were made in air masses free from local, coastal influence, and suggest that IO might be ubiquitous, albeit at low levels, in the marine boundary layer [Allan *et al.*, 2000a].

The second N(O₃) calculation method utilised the photostationary state (PSS) expression to calculate the ozone production term (see Chapter 4 for details), and may be represented by

$$N(O_3) = j(NO_2)[NO_2] - k_{25}[NO][O_3] - \{fj(O^1D) + k_2[OH] + k_3[HO_2]\}[O_3] \quad (5.24)$$

where $j(NO_2)$ is the photolysis rate of NO₂, and k_{25} is the rate coefficient for reaction (5.25):



The results of all three sets of calculations are presented in the form of a time series in Figure 5.9. The most striking thing about Fig. 5.9 is that the PSS derived N(O₃) values were systematically much higher than those derived from the peroxy radical measurements, as found for the EASE campaign calculations (see Chapter 4 for more discussion of this point). The range of values from the PSS expression was (0.0-3.1) ppbv h⁻¹, as opposed to (-0.2)-(+0.2) ppbv h⁻¹ from the peroxy radical data. It is also interesting that the peroxy radical measurements implied that ozone production and destruction were very finely balanced at Cape Grim throughout SOAPEX 2. This finding is in contrast to the EASE campaigns, where periods close to the balance point (compensation point) were interspersed with much more polluted episodes, when N(O₃) reached values of several ppbv h⁻¹.

Table 5.9 gives the mean daytime (06:00-19:00 AEST) ozone tendencies from averaged diurnal cycles using the data subdivisions described in Section 5.4. It is noteworthy that the range of values across all data subdivisions was very small [(-0.12)-(-0.04) ppbv h⁻¹]; no positive mean ozone tendency was calculated for any data set, whether 'clean' or 'semi-polluted'. The trend to more negative ozone tendencies with increasing HCHO/CO is

puzzling, especially given the increasing NO mixing ratios across the bins (Table 5.6c), although again it must be emphasised that the range of $N(O_3)$ values was very small [(-0.10)-(-0.04) ppbv h^{-1} ; cf. day-by-day analysis].

Figure 5.9 Ozone tendencies during SOAPEX 2 (06:00-19:00 AEST daytime means)

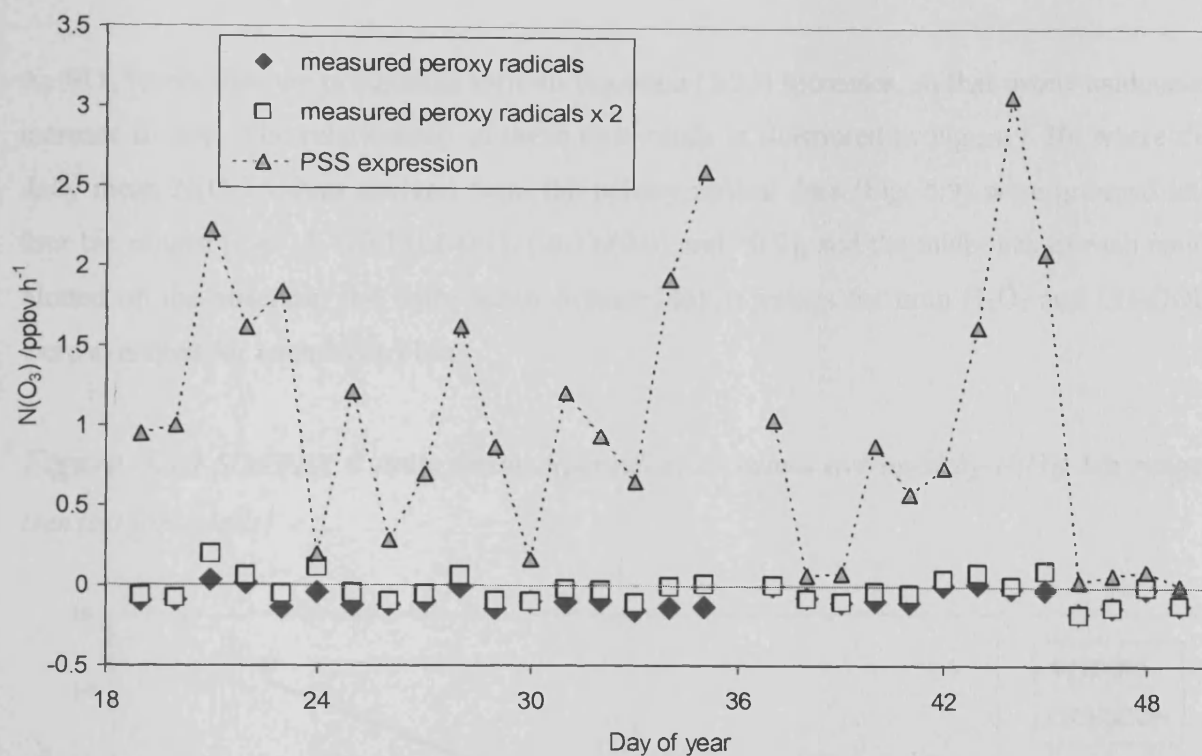
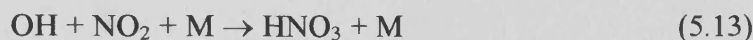


Table 5.9 Mean daytime ozone tendencies calculated from Equation (5.23) for each data subdivision during SOAPEX 2 (see Section 5.4 for details)

Data subdivision		$N(O_3) / \text{ppbv } h^{-1}$
Trajectory	Baseline	-0.12
	Non-baseline	-0.06
Wind direction	$>150^\circ$	-0.10
	$<150^\circ$	-0.06
HCHO/CO	<0.0035	-0.04
	0.0035-0.005	-0.07
	0.005-0.007	-0.08
	>0.007	-0.10
Toluene/benzene	<0.4	-0.09
	0.4-0.55	-0.09
	0.55-0.7	-0.08
	>0.7	-0.05

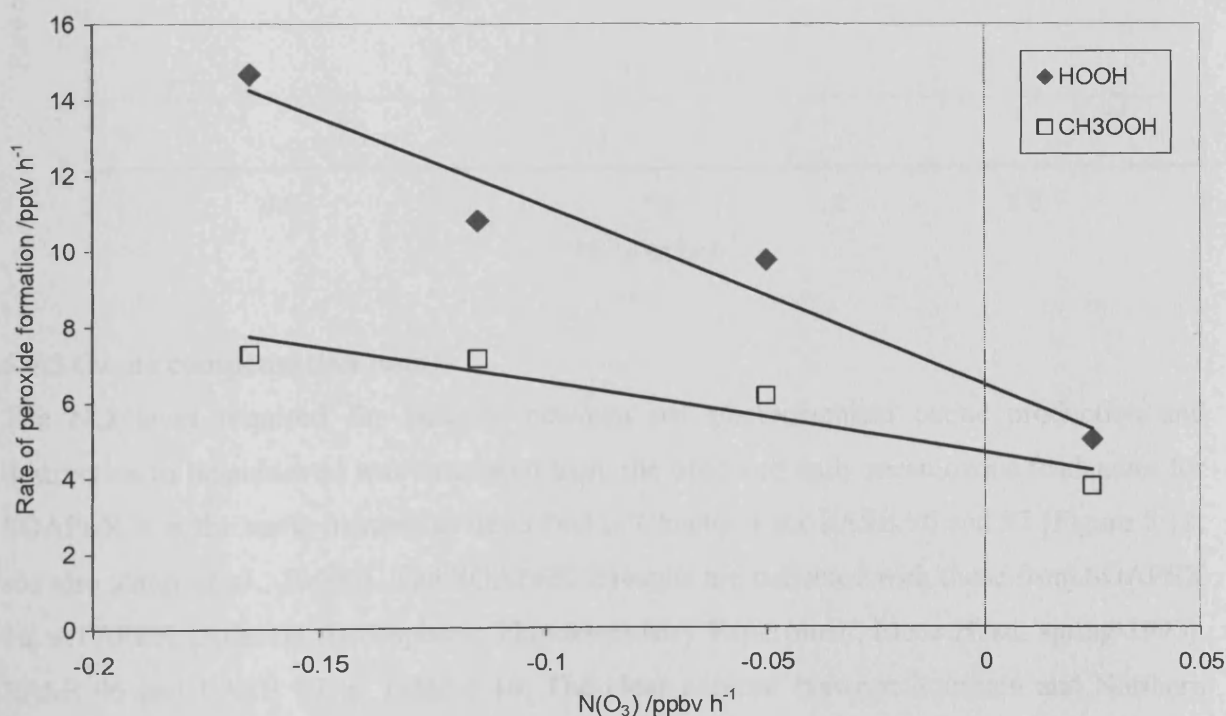
5.5.2 Peroxide production and ozone tendency

As discussed in Section 5.4.2, the rate of peroxide production is expected to be less in 'semi-polluted' air than in 'clean' air, as reaction with NO_x becomes the dominant loss pathway for RO_x ($\text{OH} + \text{HO}_2 + \text{RO}_2$), in particular *via* reaction (5.13):



As NO_x levels rise, the production term in Equation (5.23) increases, so that ozone tendencies increase in turn. The relationship of these two trends is illustrated in Figure 5.10, where the daily mean $\text{N}(\text{O}_3)$ values derived from the peroxy radical data (Fig. 5.9) were grouped into four bin ranges [<-0.13 , $(-0.13)-(-0.1)$, $(-0.1)-(-0.0)$ and >0.0], and the midpoints of each range plotted on the abscissa; the daily mean $\Delta(\text{peroxide})/\Delta t$ values for both H_2O_2 and CH_3OOH were averaged for each $\text{N}(\text{O}_3)$ bin.

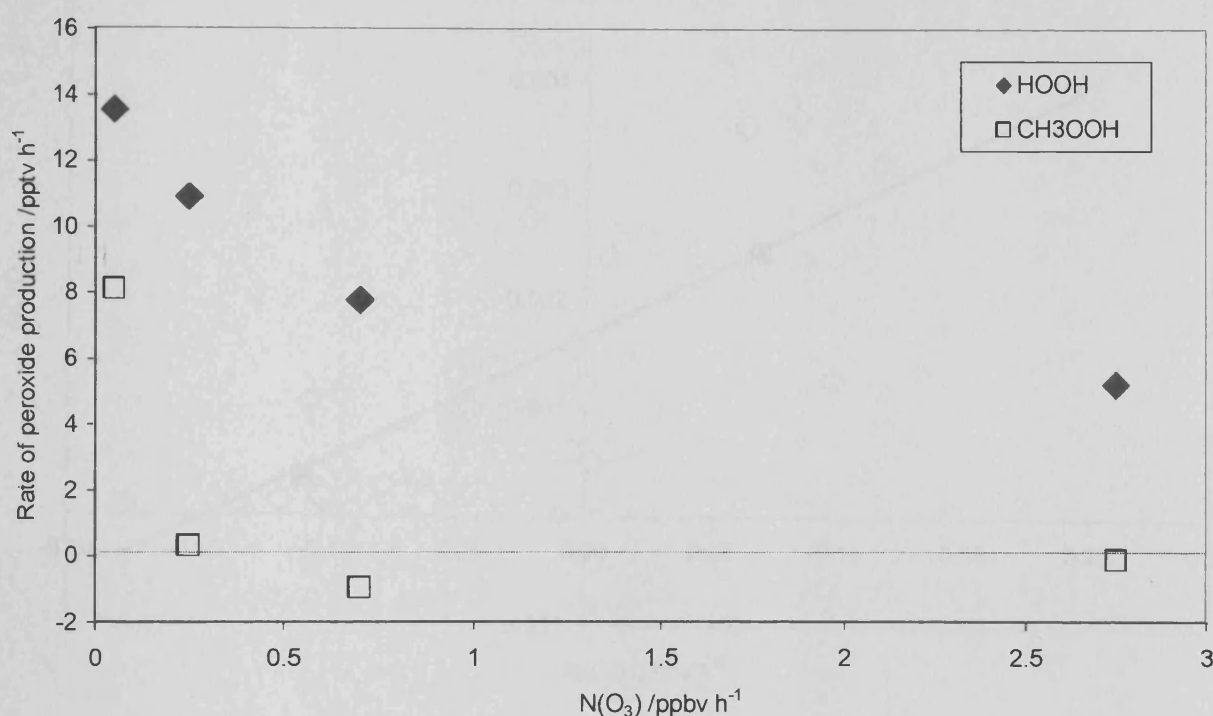
Figure 5.10 SOAPEX 2 daily mean $\Delta(\text{peroxide})/\Delta t$ values averaged by $\text{N}(\text{O}_3)$ bin ranges (see text for details)



Qualitatively, Fig. 5.10 shows that the rate of production of both hydrogen and organic peroxide diminished as ozone tendency increased. The results of a similar analysis for EASE 97 are presented in Figure 5.11. The same general trend is observed as in Fig. 5.10, although the $\text{N}(\text{O}_3)$ range is of course considerably shifted (essentially from negative to positive). It is

worth noting that in each plot the rates of peroxide production in the 'cleanest' air masses were similar: *ca* 14 pptv h⁻¹ for H₂O₂ and *ca* 8 pptv h⁻¹ for CH₃OOH, despite the different conditions encountered. Interestingly, in EASE 97, CH₃OOH production appeared to virtually cease in more polluted air (N(O₃) values greater than about 0.2 ppbv h⁻¹), whereas significant H₂O₂ production was still observed (*ca* 4 pptv h⁻¹).

Figure 5.11 EASE 97 daily mean $\Delta(\text{peroxide})/\Delta t$ values averaged by N(O₃) bin ranges (see text for details)

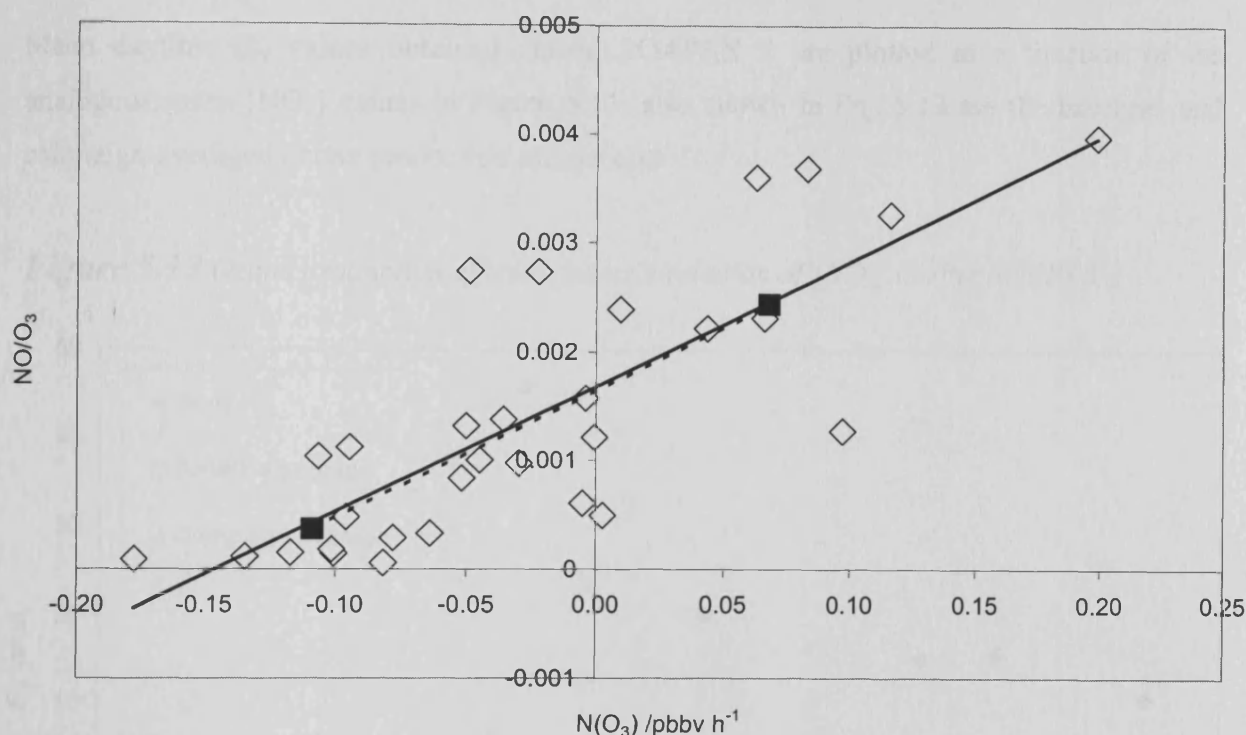


5.5.3 Ozone compensation point

The NO level required for balance between net photochemical ozone production and destruction to be achieved was estimated from the observed daily mean ozone tendencies for SOAPEX 2 in the same manner as described in Chapter 4 for EASE 96 and 97 [Figure 5.12; see also *Zanis et al.*, 2000b]. The SOAPEX 2 results are collected with those from SOAPEX 1a, ATAPEX (Atlantic Atmospheric Photochemistry Experiment, Mace Head, spring 1995), EASE 96 and EASE 97 in Table 5.10. The clear contrast between Southern and Northern Hemisphere compensation point estimates obtained by *Carpenter et al.* [1997] (55 pptv NO for ATAPEX, 23 pptv NO for SOAPEX 1a) was not observed in the data from the EASE and SOAPEX 2 campaigns (40 pptv NO for both EASE 97 and SOAPEX 2). As discussed in Chapter 4, the derived compensation point estimates depend critically on the peroxy radical mixing ratios used in the calculations (see also Chapter 6); in addition, the high degree of

scatter in the plots of $N(O_3)$ versus NO/O_3 is reflected in the large error limits in the compensation point estimates (see plots shown in Chapter 4). Perhaps the main conclusion to be drawn from these results, together with those presented for EASE 96 and EASE 97 in Chapter 4, is that the ozone compensation point is difficult to define from experimental data with precision; a range of $[NO]$ values is probably more safely quoted than a single number.

Figure 5.12 Scatter plots of mean daytime $N(O_3)$ versus NO/O_3 for SOAPEX 2^a



^a This Figure uses $N(O_3)$ values from the peroxy radicals as measured. The solid lines represent the standard linear regression lines of best fit to the data; the dashed lines with filled squares are the lines of best fit using the organic correlation method, which takes into account errors in both dependent and independent variables [e.g., Zanis *et al.*, 2000b]. The latter line is used to derive estimates for the ozone compensation point ($N(O_3) = 0$; see text for details).

Table 5.10 Ozone compensation point values ($N(O_3)=0$) for SOAPEX 1a, 2, ATAPEX, EASE 96 and EASE 97 estimated by plotting the daily averaged $N(O_3)$ values calculated from measured peroxy radicals versus the daily averaged NO/O_3 ratio

Campaign	Measured peroxy radicals ^a	Peroxy radicals $\times 2^a$
ATAPEX ^{b,c}	55 $\pm$ 30	-
EASE 96	35 $\pm$ 30	18 $\pm$ 13
EASE 97	40 $\pm$ 21	22 $\pm$ 18
SOAPEX 1a ^c	23 $\pm$ 20	-
SOAPEX 2	40 $\pm$ 23	28 $\pm$ 19

^a Compensation points are in pptv NO; error limits for EASE/SOAPEX 2 calculated as described in Chapter 4.

^b Mace Head, spring 1995.

^c Values taken from Carpenter *et al.* [1997]; compensation points estimated from range of $[NO]$ values observed in periods of net ozone destruction/production.

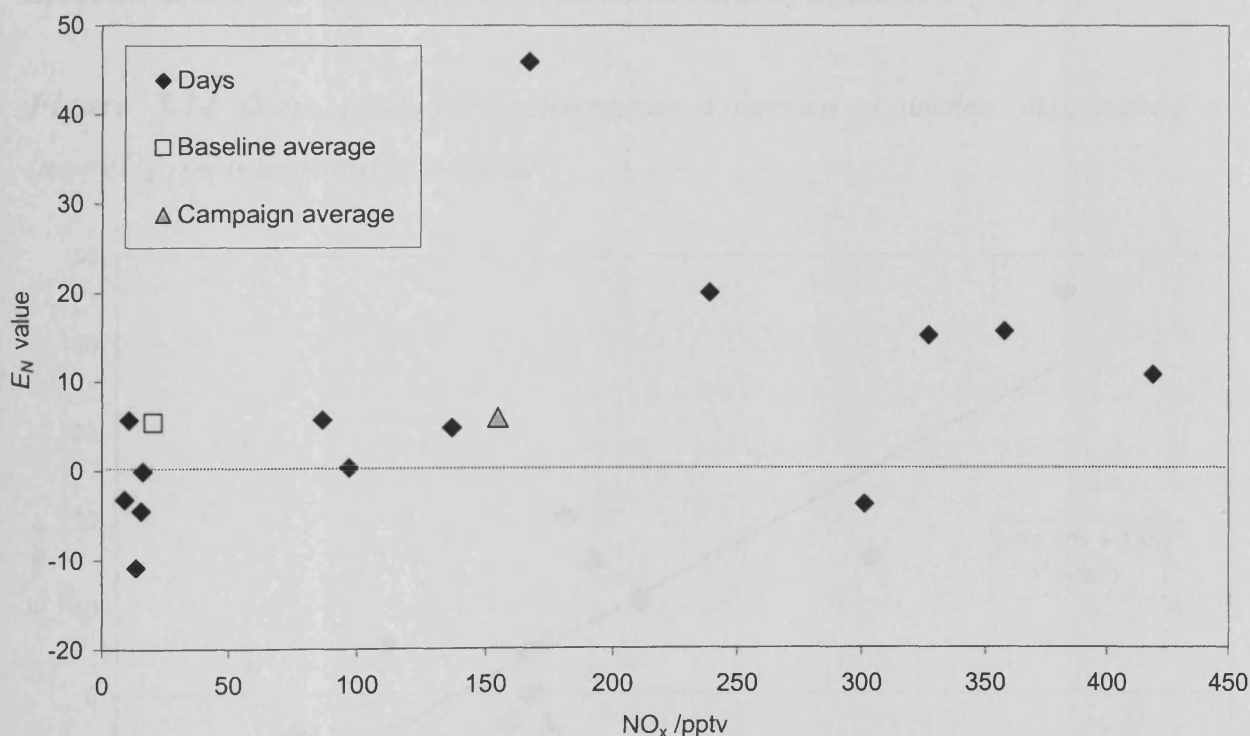
5.5.4 Ozone production efficiency

As discussed previously in Chapter 4, the ozone production efficiency (E_N) may be defined as the number of molecules of ozone produced per molecule of NO_x oxidised to an NO_z species [Liu *et al.*, 1987], and is given by:

$$E_N = \frac{\Delta\text{O}_3}{\Delta(\text{NO}_y - \text{NO}_x)} \quad (5.26)$$

Mean daytime E_N values obtained during SOAPEX 2 are plotted as a function of the analogous mean $[\text{NO}_x]$ values in Figure 5.13; also shown in Fig. 5.13 are the baseline- and campaign-averaged ozone production efficiencies.

Figure 5.13 Ozone production efficiencies as a function of $[\text{NO}_x]$ during SOAPEX 2

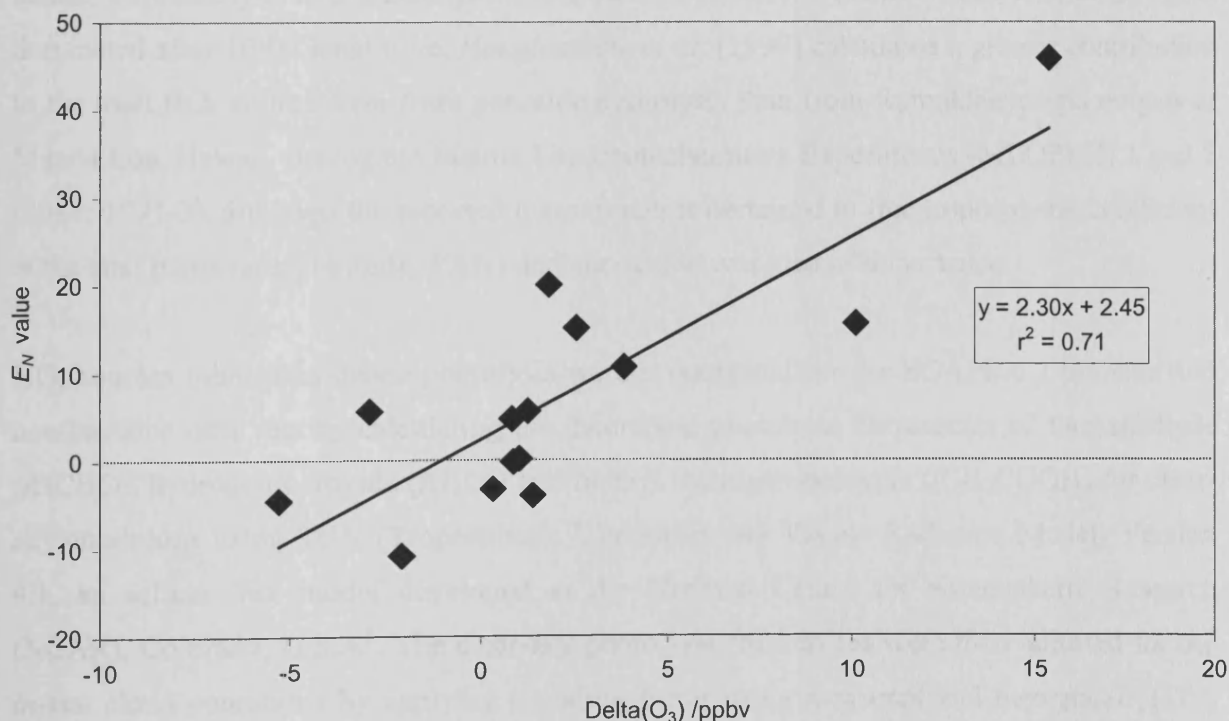


The data in Fig. 5.13 show that below *ca* 150 pptv NO_x , the ozone production efficiency was very low, or even negative, implying net ozone destruction (Section 5.5.1); the averaged baseline E_N value was 5.4 (at *ca* 20 pptv NO_x). Relatively high E_N values were obtained for 150-250 pptv NO_x , with a general trend to decreasing E_N with $[\text{NO}_x]$ above 150 pptv. The campaign-averaged E_N value was 5.9 (for an average 155 pptv NO_x). The range of NO_x mixing ratios observed during SOAPEX 2 was generally lower than at Mace Head during the EASE campaigns; this is reflected in the fact that the switch from relatively high ozone

production efficiency to net ozone destruction was observed in the SOAPEX 2 data (Fig. 5.13), but not in the EASE data, where an unbroken trend of increasing E_N with decreasing NO_x was observed (Chapter 4, Section 4.7).

No significant correlation between ozone tendency and ozone production efficiency was observed in the SOAPEX 2 data, in contrast to EASE 97 (Chapter 4). Interestingly, however, a positive correlation between daytime ΔO_3 (defined here as $\{\text{mean}[\text{O}_3]_{17:00-19:00} - \text{mean}[\text{O}_3]_{05:00-07:00}\}$) and ozone production efficiency was observed (Figure 5.14). This result perhaps indicates the importance of transport effects in the E_N values; ozone tendency is probably a better indicator of *in-situ* chemistry than ozone production efficiency, especially where ozone production and destruction are finely balanced, as would seem to be the case at Cape Grim for much of the time in summer. Transport of ozone and NO_y to Cape Grim might therefore also explain why positive E_N values were often observed during SOAPEX 2 where net ozone destruction was inferred from the ozone tendency calculations (Fig. 5.9).

Figure 5.14 Ozone production efficiency as a function of daytime ΔO_3 , defined as $\{\text{mean}[\text{O}_3]_{17:00-19:00} - \text{mean}[\text{O}_3]_{05:00-07:00}\}$



5.6 SOAPEX 2 Daytime HO_x Sources and Sinks

5.6.1 Daytime HO_x sources other than ozone photolysis[†]

Many recent studies have focussed on the importance of HO_x (OH+HO₂) sources other than ozone photolysis in the relatively dry upper troposphere, particularly peroxide, formaldehyde and acetone photolysis [*e.g.*, *Folkens et al.*, 1997; *McKeen et al.*, 1997; *Prather et al.*, 1997; *Jaeglé et al.*, 1998, 2000; *Wennberg et al.*, 1998; *Faloona et al.*, 2000]; there have been fewer assessments of alternative HO_x sources in the boundary layer. *Kleinman et al.* [1995] reported a significant contribution from the photolysis of carbonyl compounds, particularly formaldehyde, to the HO_x source budget at a forested, rural site in Georgia, U.S.A., during the Southern Oxidant Study 2 (SOS 2) in 1992 (mean HCHO contribution 27%; mean contribution of other carbonyls 14%); the photolysis of ozone was estimated to contribute just 55% to the total HO_x production, on average. (Typical daytime mixing ratios of salient species during SOS 2 were as follows: ozone 30-60 ppbv, formaldehyde 2-4 ppbv, NO 50-300 pptv, NO₂ 0.5-2 ppbv.) *George et al.* [1999] reported the following modelled HO_x sources in polluted Los Angeles air during the Los Angeles Free Radical Experiment (LAFRE), 1993, in descending order of importance: photolyses of nitrous acid (HONO; primarily before noon), ozone, formaldehyde and dialdehydes, and the non-photolytic ozone-alkene reactions, which dominated after 16:00 local time. *Hauglustaine et al.* [1999] calculated a greater contribution to the total HO_x source term from peroxide photolysis than from formaldehyde photolysis at Mauna Loa, Hawaii, during the Mauna Loa Photochemistry Experiments (MLOPEX) 1 and 2 (1988; 1991-2), although the reported measurements pertained to free tropospheric conditions at the site; peroxyacetyl nitrate (PAN) decomposition was also of importance.

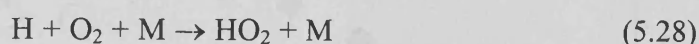
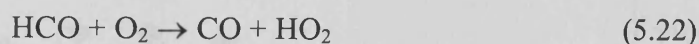
HO_x sources other than ozone photolysis were investigated for the SOAPEX 2 baseline and non-baseline data sets by calculating the theoretical photolysis frequencies of formaldehyde (*j*HCHO), hydrogen peroxide (*j*H₂O₂) and methyl hydrogen peroxide (*j*CH₃COOH) for clear-sky conditions using TUV (Tropospheric Ultraviolet and Visible Radiation Model) Version 4.1, an actinic flux model developed at the National Center for Atmospheric Research (NCAR), Colorado, U.S.A.[‡]. The clear-sky photolysis frequencies were then adjusted for the *in-situ* cloud conditions by applying a scaling factor using measured and theoretical (TUV, clear-sky) *j*(NO₂) values:

[†] Discussion of HO_x production from ozone and nitrate radical reactions with alkenes during SOAPEX 2 is deferred until Section 5.8.

[‡] TUV was kindly run on my behalf by Gavin Edwards, University of Leicester.

$$j(\text{'meas'}) = j(\text{TUV,clear-sky}) * j(\text{NO}_2)_{\text{meas}} / j(\text{NO}_2)_{\text{TUV,clear-sky}} \quad (5.27)$$

Each photolytic process was assumed to produce two free radicals, so that derivation of the photolysis rates was equivalent to a HO_x rate of production analysis:



Composite baseline and non-baseline diurnal cycles were then calculated for each photolysis rate as described previously for the measured variables (Section 5.4.1). The percentage contributions of the photolyses of ozone, formaldehyde, hydrogen peroxide and methyl hydrogen peroxide to the total HO_x production rate derived from these calculations are shown in Figure 5.15, where (a) is baseline, (b) non-baseline. (The legend in Panel (b) of Fig. 5.15 applies to both panels.)

Fig. 5.15 shows that ozone photolysis dominated daytime HO_x production during SOAPEX 2 for both baseline and non-baseline conditions (mean percentage contributions for the daytime period 06:00-19:00 hours 73% and 78%, respectively). The only other important contributor was formaldehyde photolysis (mean daytime contributions 20% and 17%, respectively). The peroxide contribution was always <10% for both data sets. The only striking difference observed between baseline and non-baseline conditions was the smaller total rate of HO_x production in the baseline average diurnal cycle (peak values *ca* 3.5x10⁶ molecules cm⁻³ s⁻¹ for baseline, 5.0x10⁶ molecules cm⁻³ s⁻¹ for non-baseline). This effect was largely (>80%) due to higher HO_x production from ozone photolysis in non-baseline conditions *via* reaction (5.31), which in turn could be traced to the significantly higher mean specific humidity in the non-baseline data set (7.3 g kg⁻¹ for baseline, 10.4 g kg⁻¹ for non-baseline). A similar difference in humidity between baseline and semi-polluted conditions was observed during SOAPEX 1 [Carpenter *et al.*, 1997].

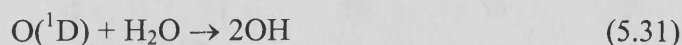
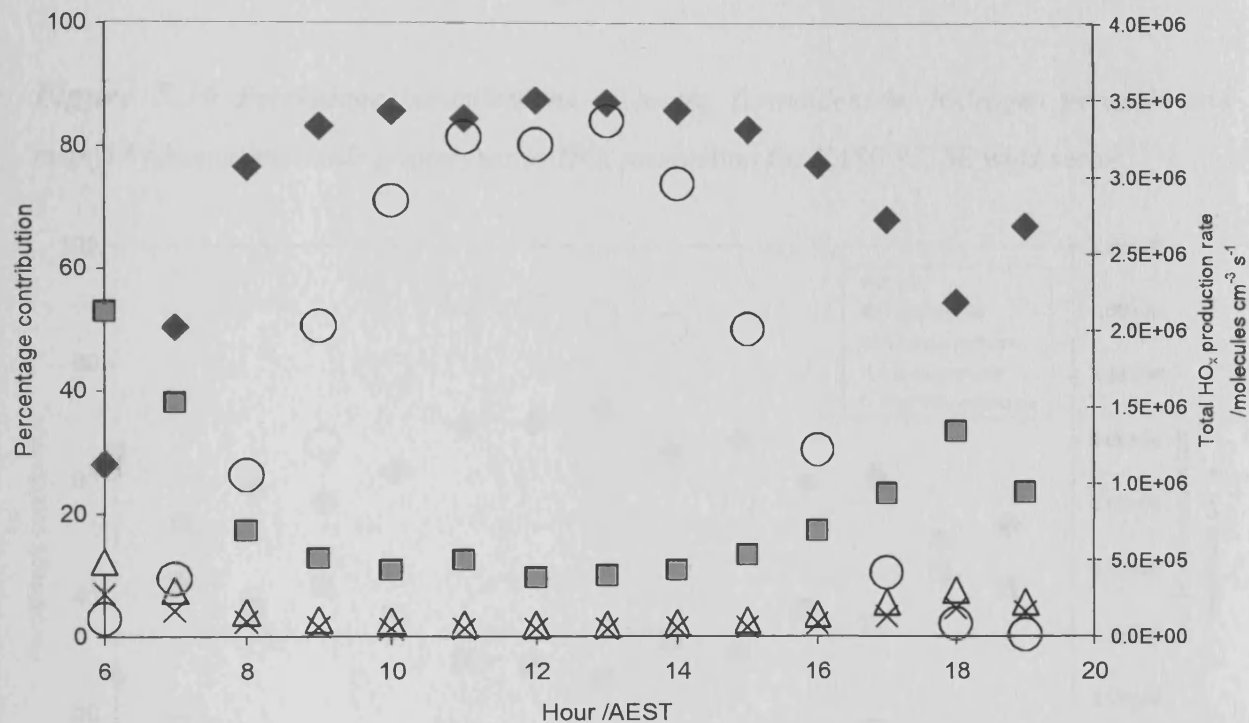
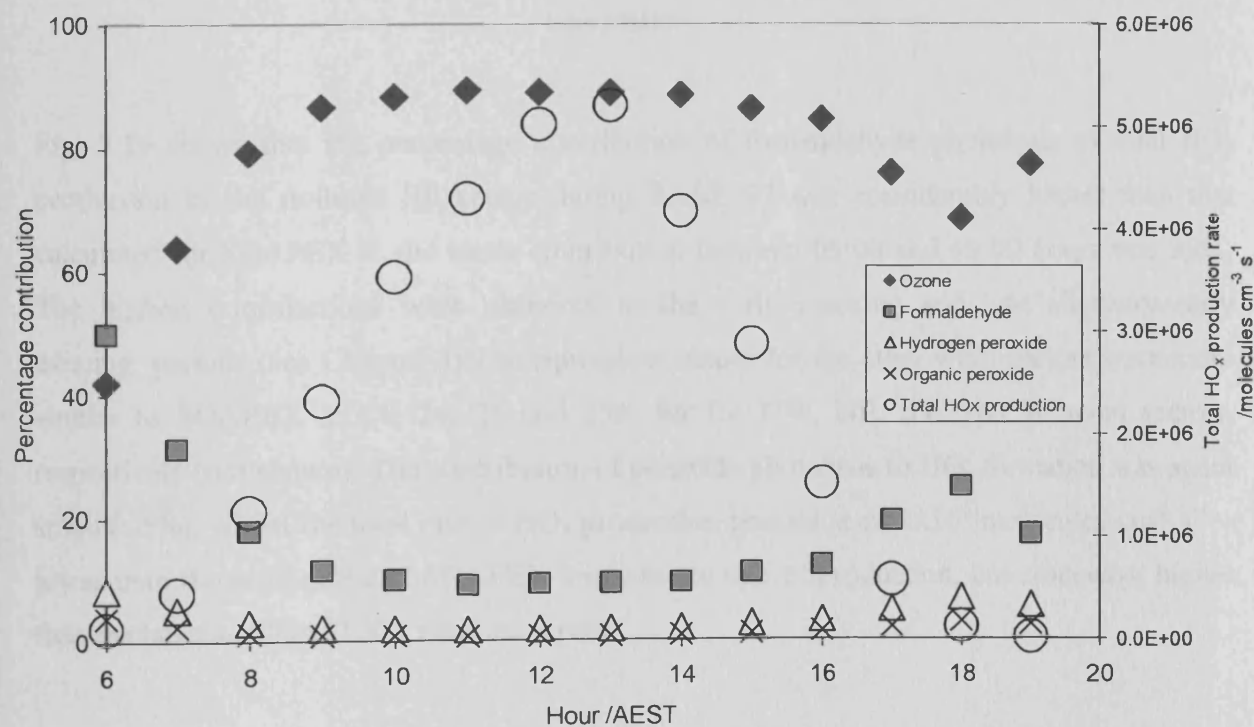


Figure 5.15 Percentage contributions of ozone, formaldehyde, hydrogen peroxide and methyl hydrogen peroxide photolyses to HO_x production during SOAPEX 2

(a) Baseline



(b) Non-baseline



5.6.2 HO_x sources: comparison with EASE 97

The same procedure as described in the last section for calculating contributions of photolabile compounds other than ozone to total HO_x production was carried out for the EASE 97 data set, using the wind sector classification described in Chapter 4. The results for the south-east (SE) wind sector are presented in Figure 5.16.

Figure 5.16 Percentage contributions of ozone, formaldehyde, hydrogen peroxide and methyl hydrogen peroxide photolyses to HO_x production for EASE 97, SE wind sector

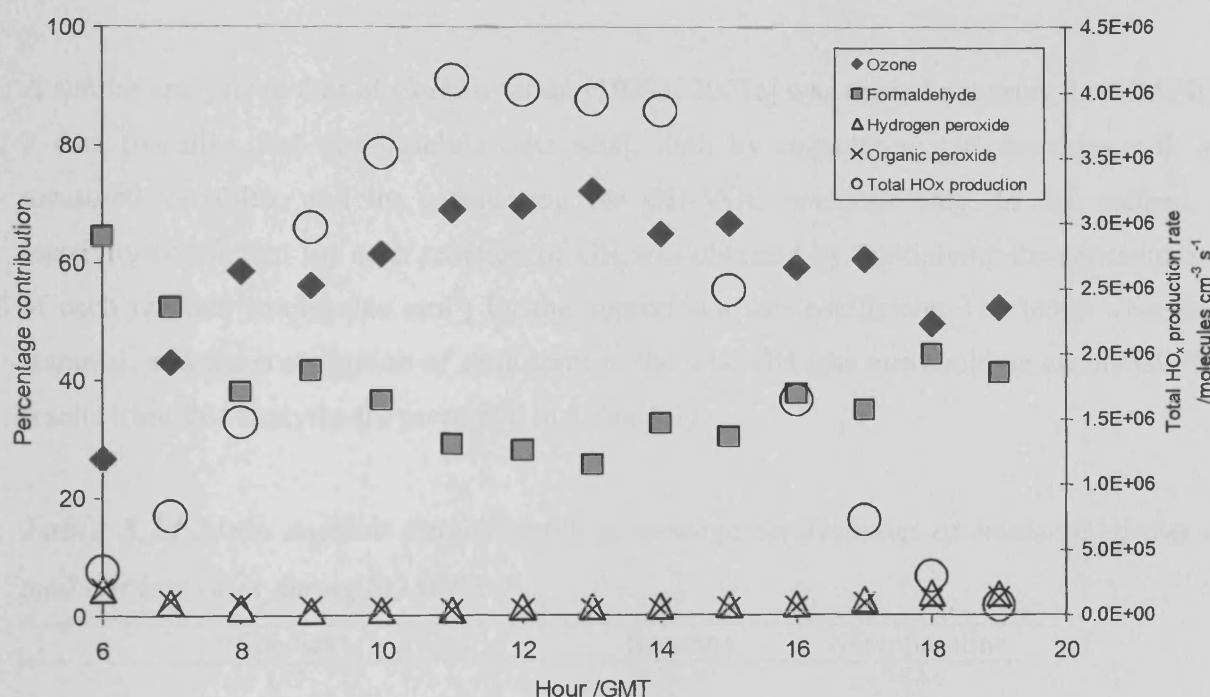


Fig. 5.16 shows that the percentage contribution of formaldehyde photolysis to total HO_x production in the polluted SE sector during EASE 97 was considerably higher than that calculated for SOAPEX 2: the mean contribution between 06:00 and 19:00 hours was 38%. The highest contributions were observed in the early morning and late afternoon/early evening periods (see Chapter 3). The equivalent values for the other wind sectors were more similar to SOAPEX 2: 24, 24, 23 and 25% for the NW, NE, SW and W wind sectors, respectively (not shown). The contribution of peroxide photolysis to HO_x formation was again small (<5%), whilst the total rate of HO_x production peaked at *ca* 4×10^6 molecules cm⁻³ s⁻¹ – lower than the semi-polluted SOAPEX 2 maximum rate of production, but somewhat higher than the baseline SOAPEX 2 maximum rate.

5.6.3 OH loss reactions during SOAPEX 2

Carslaw et al. [1999a] calculated the percentage contributions of a wide range of OH reactions to the total OH loss rate during the EASE 96 campaign for both 'clean' and semi-polluted conditions. By far the most important OH loss process was reaction with CO (52.8% in 'clean' air, 44.6% in semi-polluted air; 24-hour averages), followed by reaction with CH₄ (21.0%, 12.9%) and NO₂ (4.8%, 14.7%). Between 65% and 90% of the OH losses on each day during the campaign could be attributed to the reactions with CO and CH₄ only. *Carslaw et al.* [2001a] found that 80-95% of the OH-VOC losses during EASE 97 were accounted for by the CO and CH₄ reactions only.

A similar analysis to that of *Carslaw et al.* [1999a, 2001a] was carried out using the SOAPEX 2 data (baseline and non-baseline data sets), both by considering OH reactions with all measured variables, and by considering the OH-VOC reactions only. In this method, a reactivity coefficient for each reaction of OH was obtained by multiplying the concentration of each reactant (molecules cm⁻³) by the appropriate rate coefficient. The terms were then summed, and the contribution of each term to the total OH loss rate could be examined. The results from this analysis are presented in Table 5.11.

Table 5.11 Mean daytime (06:00-19:00) percentage contributions of measured species to total OH loss rates during SOAPEX 2

Species	Baseline	Non-baseline
CO	36.3	33.6
CH ₄	27.4	26.3
HCHO	7.4	6.9
HOOH	1.1	1.0
CH ₃ OOH	2.6	2.4
Iso-butene	6.0	5.8
1,3-butadiene	2.0	1.9
Isoprene	4.4	4.4
DMS	1.2	1.1
O ₃	3.3	3.1
NO	0.05	0.4
NO ₂	0.5	5.5
Total CO+CH ₄ contribution (Percentage of all loss routes)	61.2	57.8
Total CO+CH ₄ contribution (Percentage of VOC loss routes only)	63.6	62.9

Table 5.11 shows that the contribution of CO and CH₄ to the total OH loss rate during SOAPEX 2 was considerably lower than that observed during the EASE campaigns. This effect is largely attributable to the much lower CO mixing ratios at Cape Grim than at Mace Head (campaign mean values 44 ppbv for SOAPEX 2, 111 ppbv for EASE 96, 156 ppbv for

EASE 97). Indeed, the CO contribution to OH loss averaged less than 40% for SOAPEX 2, which contrasts with the EASE 96 24-hour mean value of *ca* 50% [Carslaw *et al.*, 1999a]; the percentage OH+VOC loss attributable to CO during EASE 97 was in the range 60-70% [Carslaw *et al.*, 2001a].

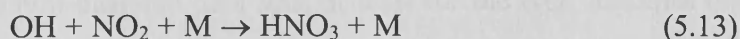
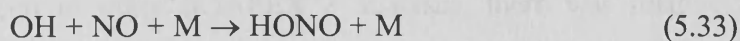
The contributions of particular species to OH loss during SOAPEX 2 were generally similar for baseline and non-baseline conditions, although the OH+NO₂ reaction clearly became more significant in semi-polluted air.

5.7 The NO_x Balance During SOAPEX 2: Comparison with EASE 97

As seen in previous sections of this chapter, the NO_x levels during SOAPEX 2 were low, in both baseline and 'semi-polluted' conditions, compared with those generally observed in the Northern Hemisphere, even at a relatively remote site such as Mace Head (see Chapter 4). For example, typical daytime NO_x mixing ratios were of the order of 30 pptv in non-baseline air masses during SOAPEX 2, compared with *ca* 100 pptv in the 'clean' sectors during EASE 96. Even in the cleanest, baseline air, however, measurable levels of NO, albeit very low (2 pptv), were recorded. In order to investigate these observations further, chemical lifetimes of NO_x were calculated for SOAPEX 2 baseline and non-baseline conditions, as well as for EASE 97 (by wind sector), assuming that the main loss processes for NO_x are the reactions of OH with both NO and NO₂. The lifetime (τ) of each species with respect to OH reaction is then given by:

$$\tau = 1/k[\text{OH}] \quad (5.32)$$

where k is the rate coefficient for either reaction (5.33) (NO) or (5.13) (NO₂):



Since NO and NO₂ are rapidly interconverted in the daytime, through the reaction sequence comprising the photostationary state (see Chapter 4), the lifetime of NO_x may be then be calculated from Equation (5.34) [*e.g.*, Brasseur *et al.*, 1999, pp.112-4]:

$$1/\tau_{\text{NO}_x} = 1/\tau_{\text{NO}} + 1/\tau_{\text{NO}_2} \quad (5.34)$$

Given τ_{NO_x} , it is possible to estimate the production or emission rate of NO_x necessary to sustain the observed NO_x mixing ratios for a given set of conditions, using an alternative definition of the lifetime of NO_x [e.g., Wayne, 2000, p. 137]:

$$\tau_{\text{NO}_x} = [\text{NO}_x]/(\text{P}_{\text{NO}_x}) \quad (5.35)$$

where P_{NO_x} is the rate of production of NO_x , which of course rearranges to give

$$\text{P}_{\text{NO}_x} = [\text{NO}_x]/\tau_{\text{NO}_x} \quad (5.36)$$

The calculations presented in this section utilised the daytime (06:00-19:00) mean FAGE OH radical measurements taken during each campaign (University of Leeds); the rate coefficients used were the JPL recommendations for the mean daytime temperatures measured in each case [DeMore *et al.*, 1997]. The results of this analysis for both SOAPEX 2 and EASE 97 are given in Table 5.12.

Table 5.12 Daytime (06:00-19:00) mean NO_x lifetimes and estimated rates of NO_x emission/production during SOAPEX 2 and EASE 97

Campaign		$\tau_{\text{NO}}/\text{h}$	$\tau_{\text{NO}_2}/\text{h}$	$\tau_{\text{NO}_x}/\text{h}$	$\text{P}_{\text{NO}_x}/\text{pptv h}^{-1}$
SOAPEX 2	Baseline	45.0	35.8	19.9	1.0
	Non-baseline	49.4	39.7	22.1	8.5
EASE 97	NW	22.0	21.5	12.1	21.7
	NE	14.5	11.3	6.4	42.6
	SE	28.1	22.1	12.4	101.2
	SW	37.8	29.7	16.6	15.1
	W	20.5	16.0	9.0	25.3

Table 5.12 shows that the estimated production rate necessary to sustain the observed NO_x mixing ratios was much lower at Cape Grim than at Mace Head: just 1 pptv h^{-1} for SOAPEX 2 baseline conditions. As seen in other SOAPEX 2 analyses, there was relatively little difference in the baseline and non-baseline data sets, at least for the NO_x lifetimes obtained, although the rate of production calculated to be necessary to sustain the observed $[\text{NO}_x]$ was significantly higher for non-baseline conditions. The NO_x lifetimes were longer for SOAPEX 2 than for EASE 97, although this is more easily seen by consideration of τ_{NO} and τ_{NO_2} in isolation. By far the longest NO_x lifetimes during EASE 97 were observed in the relatively clean SW sector, whilst the highest estimated P_{NO_x} values were obtained for the polluted SE sector, as might be expected. In general, the variation in NO_x lifetimes between the EASE 97

wind sectors is somewhat difficult to interpret, but is perhaps not surprising given the variation in $[\text{NO}_x]$, $[\text{OH}]$ and average temperature between sectors (see Table 4.3).

5.8 SOAPEX 2 Night-time Chemistry

5.8.1 Introduction

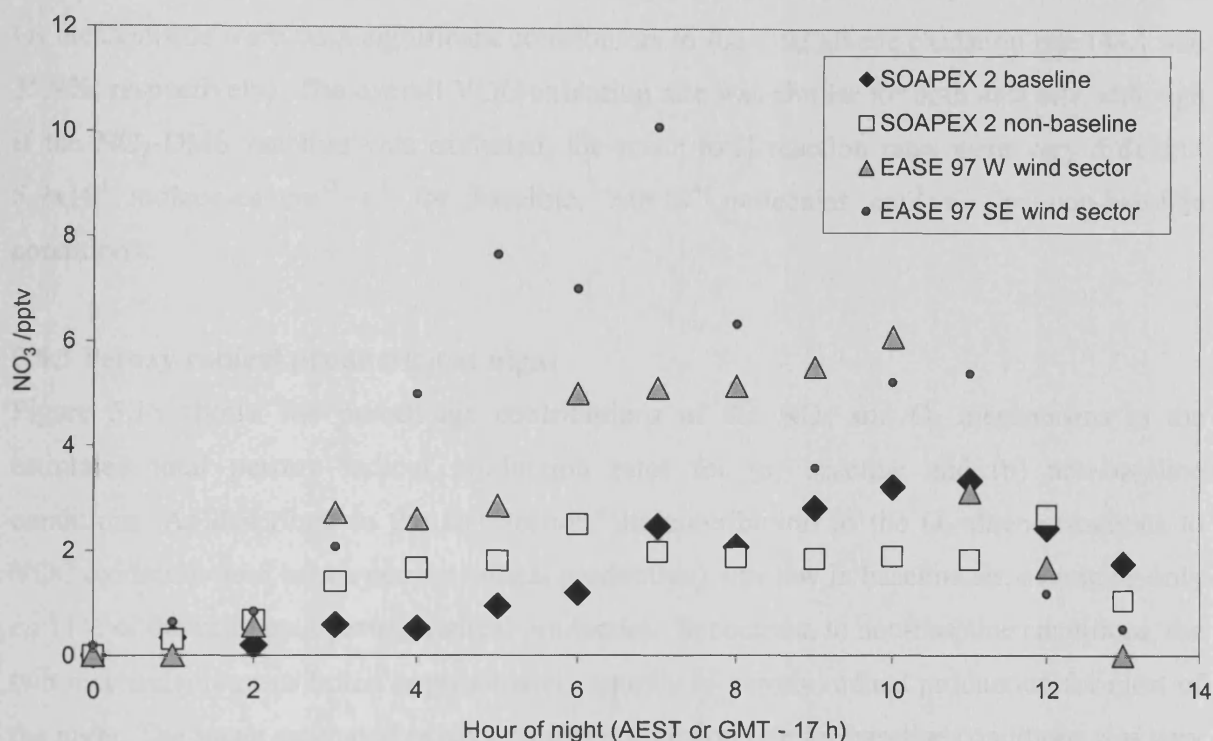
As mentioned in the introduction to Chapter 3, during SOAPEX 1a (austral summer 1995) in baseline conditions only very low night-time mixing ratios (*ca* 1 pptv) of peroxy radicals were observed; the measured levels could be explained by the persistence into night-time of CH_3O_2 radicals produced during the day, with a calculated lifetime of over 12 h [Monks *et al.*, 1996]. No significant production of peroxy radicals from reactions of ozone and/or the nitrate radical (NO_3) with alkenes at night was observed during SOAPEX 1.

The mean night-time peroxy radical mixing ratios during SOAPEX 2 were similar in baseline and non-baseline air: 1.4 and 1.5 pptv. Given the difference in humidity observed in the two sets of conditions (Section 5.6.1), it might be that the PERCA instrument underestimated the true night-time levels more in semi-polluted than in baseline conditions; this point is discussed further in Chapter 6. Figure 5.17 shows the baseline and non-baseline averaged night-time profiles of NO_3 mixing ratios during SOAPEX 2; the equivalent profiles for the EASE 97 W and SE wind sectors are also shown for comparison. The first thing to note from Fig. 5.17 is that NO_3 mixing ratios were generally somewhat lower during SOAPEX 2 than in either 'clean' or semi-polluted conditions during EASE 97, in line with the lower ozone and nitrogen dioxide levels during the former campaign (see Section 5.4.4). Interestingly, NO_3 during averaged SOAPEX 2 baseline conditions reached slightly higher mixing ratios than during 'semi-polluted' conditions (maxima 3.3 pptv and 2.6 pptv, respectively), despite the much higher NO_2 mixing ratios in the 'semi-polluted' air (means 17 and 199 pptv, respectively). Lifetime calculations (see Chapter 3, Section 3.3) showed that the average NO_3 lifetime was over 3 h (191 min) for SOAPEX 2 baseline, compared with 11 min for SOAPEX 2 non-baseline, 22 min for the EASE 97 W wind sector and 3.5 min for the EASE 97 SE wind sector.

Peroxy radical rate of production analyses (ROPAs), based on simultaneous measurements of VOCs, O_3 and NO_3 were carried out for both baseline and non-baseline data sets, as described

for EASE 97 in Chapter 3. The results of these analyses, together with a comparison of SOAPEX 2 and EASE 97 night-time chemistry, are presented in the following sections.

Figure 5.17 Averaged night-time NO_3 profiles for SOAPEX 2 and EASE 97



5.8.2 Baseline and non-baseline night-time chemistry

Table 5.13 shows the mean total night-time rates of the O_3 -alkene, NO_3 -alkene and NO_3 -DMS reactions during SOAPEX 2 (baseline and non-baseline), together with the percentage contribution of selected mechanisms to VOC oxidation.

Table 5.13 Mean night-time reaction rates during SOAPEX 2^a

Data set	$\text{NO}_3 + \text{CH}_4^b$	$\text{NO}_3 + \text{DMS}$	$\text{NO}_3 + \text{alkenes}$	$\text{O}_3 + \text{alkenes}$	O_3 contribution to alkene oxidation /%	Total VOC oxidation rate ^c	Contribution of NO_3 -DMS reaction /%
Baseline ^d	2.5×10^3	1.6×10^5	2.7×10^3	5.3×10^2	16.4	1.6×10^5	96.8
Non-baseline	1.8×10^3	8.6×10^4	2.6×10^4	3.3×10^4	55.9	1.5×10^5	58.6

^a All reaction rates are in $\text{molecules cm}^{-3} \text{s}^{-1}$.

^b Upper limits using a maximum rate coefficient of $1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [Atkinson, 1994].

^c Includes DMS.

^d The baseline figures are means of all night-time baseline hours where measurements were available (27); the non-baseline figures are the averages from a composite night-time cycle, as for EASE 97 in Chapter 3.

The first thing to note from Table 5.13 is the importance of the NO_3 -DMS reaction in both baseline and non-baseline conditions, although clearly this reaction dominated any other VOC oxidation path in the baseline night-time boundary layer. Even with an average NO_3 mixing ratio of only 1.6 pptv, the NO_3 -alkene reactions dominated alkene oxidation in baseline conditions (83.6%).[†] The picture was more complex in non-baseline air, where the NO_3 and O_3 mechanisms were both significant contributors to the total alkene oxidation rate (44.1 and 55.9%, respectively). The overall VOC oxidation rate was similar for both data sets, although if the NO_3 -DMS reaction was excluded, the mean total reaction rates were very different: $5.9 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$ for baseline, $7.0 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$ for non-baseline conditions.

5.8.3 Peroxy radical production at night

Figure 5.18 shows the percentage contributions of the NO_3 and O_3 mechanisms to the estimated total peroxy radical production rates for (a) baseline and (b) non-baseline conditions. As described in the last section, the contribution of the O_3 -alkene reactions to VOC oxidation (and hence peroxy radical production) was low in baseline air, averaging only *ca* 11% of the estimated peroxy radical production. In contrast, in non-baseline conditions, the two mechanisms contributed approximately equally to peroxy radical production for most of the night. The mean estimated peroxy radical production rate for baseline conditions was very low: $6.0 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$, compared to $6.7 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$ for non-baseline air. In fact, the estimated rate of peroxy radical production in baseline air was 5 times lower than non-baseline air for the NO_3 mechanism, and 50 times lower for the O_3 mechanism.

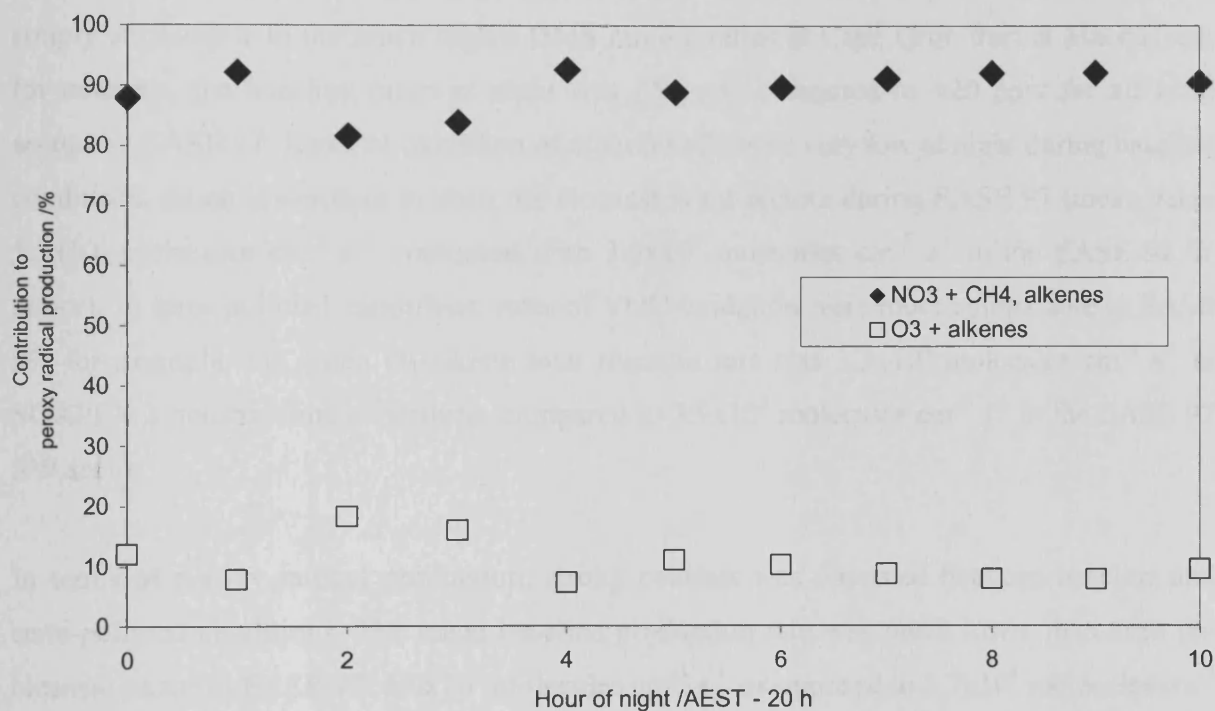
5.8.4 Daytime and night-time comparison

There is no significant oxidation of VOCs during the day by NO_3 reactions, as NO_3 is rapidly photolysed (see Chapter 3, Section 3.1); however, the O_3 -alkene reactions proceed during the day as well as at night. During SOAPEX 2, the mean daytime (06:00-19:00) total rate of reaction *via* the O_3 -alkene mechanism was $3.7 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$ for non-baseline conditions, similar to the night-time mean ($3.3 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$). This mean rate represents an approximate upper bound for the rate of RO_x ($\text{HO}_x + \text{RO}_2$) production *via* this mechanism (see Chapter 3). Comparison with the results presented in Section 5.6 shows that this route represented only a small percentage of the total RO_x production during the day (daytime mean total $2.2 \times 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$).

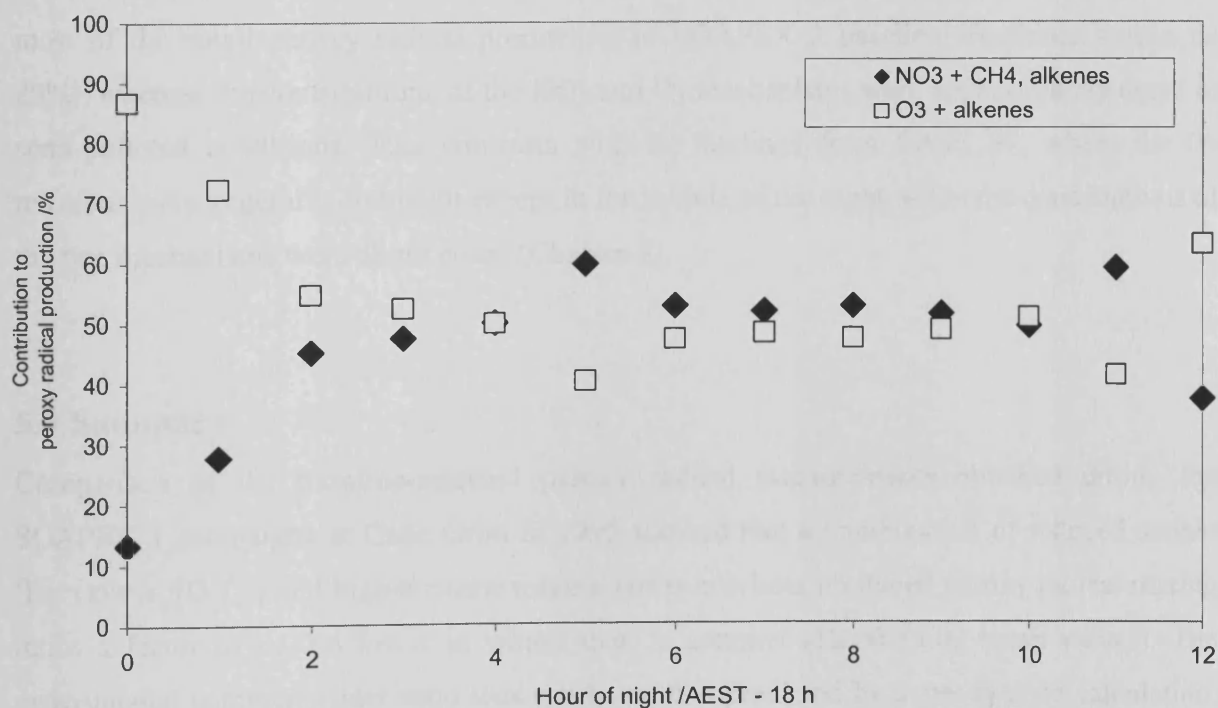
[†] Of the more reactive, C3-4 alkenes, only iso-butene was present at significant mixing ratios in baseline air at night (up to 11 pptv).

Figure 5.18 Percentage contributions of NO_3 - and O_3 -alkene reactions to total peroxy radical production rate during SOAPEX 2

(a) Baseline (mean total peroxy radical production rate $6.0 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$)^a



(b) Non-baseline (mean total peroxy radical production rate $6.7 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$)^a



^a See Section 5.8.3.

5.8.5 Comparison with EASE 97

Clearly, in terms of VOC oxidation, the NO_3 -DMS reaction was much more significant in SOAPEX 2 than in EASE 97. The mean rate of this reaction was 8.6×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$ in baseline, and 1.6×10^5 molecules $\text{cm}^{-3} \text{s}^{-1}$ for non-baseline during SOAPEX 2, compared to wind sector means in the range 1.1 – 2.6×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$ for EASE 97. This difference is simply attributable to the much higher DMS mixing ratios at Cape Grim than at Mace Head: for example, the baseline mean at night was 85 pptv, compared to <20 pptv for all wind sectors in EASE 97. Rates of oxidation of other VOCs were very low at night during baseline conditions, much lower than in even the cleanest wind sectors during EASE 97 (mean value 5.9×10^3 molecules $\text{cm}^{-3} \text{s}^{-1}$, compared with 3.0×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$ in the EASE 97 W sector). In semi-polluted conditions, rates of VOC oxidation were more comparable to EASE 97; for example, the mean O_3 -alkene total reaction rate was 3.3×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$ in SOAPEX 2 non-baseline conditions, compared to 3.9×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$ in the EASE 97 SW sector.

In terms of peroxy radical production, strong contrast was observed between baseline and semi-polluted conditions. The mean baseline production rate was much lower than even the cleanest sector in EASE 97: 6.0×10^3 molecules $\text{cm}^{-3} \text{s}^{-1}$, as opposed to 2.7×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$ in the W wind sector. In contrast, the mean production rate was estimated to be 6.7×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$ for non-baseline conditions in SOAPEX 2, compared with 4.5×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$ for the EASE 97 NW sector. The NO_3 oxidation mechanism accounted for most of the small peroxy radical production in SOAPEX 2 baseline conditions (mean *ca* 89%), whereas the contributions of the NO_3 and O_3 mechanisms were approximately equal in semi-polluted conditions. This contrasts with the findings from EASE 97, where the O_3 reactions were generally dominant except in the middle of the night, when the contributions of the two mechanisms were about equal (Chapter 3).

5.9 Summary

Comparison of the baseline-selected peroxy radical measurements obtained during the SOAPEX 1 campaigns at Cape Grim in 1995 showed that a combination of reduced actinic flux (lower $j(\text{O}^1\text{D})$) and higher ozone mixing ratios in winter produced peroxy radical mixing ratios a factor of *ca* 1.6 lower in winter than in summer (12:00–13:00 mean values). The experimental summer/winter ratio was similar to that predicted by a steady-state calculation, which assumed zero $[\text{NO}_x]$ [Penkett *et al.*, 1997].

The PERCA instrument underestimation of peroxy radical mixing ratios (see also Chapter 6) was inferred to be a factor of *ca* 2 for both the SOAPEX 1 campaigns [Monks *et al.*, 1998; 2000]. Analogous analyses for the SOAPEX 2 data set gave conflicting results: calculation of the combined rate coefficient for the peroxy radical self- and cross-reactions (k') from the experimental data implied a factor of 2.2 underestimation, whereas calculation of the midday peroxy radical mixing ratios based on the rate of production of hydrogen and organic peroxides suggested little or no humidity correction was necessary. Consequently, further analyses using the SOAPEX 2 peroxy radical data set were carried out using peroxy radical mixing ratios multiplied by a factor of two as well as using those as measured (*cf.* Chapter 4). Comparison of the PERCA [HO₂+RO₂] measurements with the University of Leeds FAGE [HO₂] measurements showed a high degree of correlation ($r^2 = 0.77$), with a mean HO₂/RO₂ ratio of 0.59.

Four different air mass classification schemes for SOAPEX 2 were compared, using (1) a combination of back trajectories and acetylene and chloroform mixing ratios; (2) incident wind direction at Cape Grim; (3) HCHO/CO ratios; and (4) toluene/benzene ratios. The first of these classifications, as developed by Dr Lucy Carpenter of the University of East Anglia[†] [see also Lewis *et al.*, 2001], was found to differentiate most clearly very clean air off the Southern Ocean from 'semi-polluted' air from Tasmania or mainland Australia, although pollution tracers, such as NO_x, were low even in the 'semi-polluted' conditions compared to those observed at Mace Head in the EASE campaigns. Neither ozone nor carbon monoxide levels were differentiated strongly by any of the four classification methods; the mixing ratio range of both species was relatively small throughout SOAPEX 2. The usefulness of the HCHO/CO and toluene/benzene ratios to segregate the SOAPEX 2 data proved fairly limited, although the HCHO/CO analysis provided the largest range of mean ozone mixing ratios (15–21 ppbv; see Table 5.6 (c)). The rates of peroxide production, as well as the peroxide production efficiencies, with respect to NO_x oxidation to NO_z, were higher in baseline air than in 'semi-polluted' air. Formaldehyde production appeared to be significant relative to NO_x oxidation across all data subdivisions.

Ozone tendency calculations (see also Chapter 4) showed that daytime ozone production and destruction were finely balanced for much of SOAPEX 2, whether the peroxy radical mixing ratios were used as measured or multiplied by a factor of two; little contrast was observed between baseline and non-baseline conditions (daytime mean N(O₃) values –0.12 and –0.06

[†] Now at the University of York.

ppbv h⁻¹, respectively). The degree of correlation between [HO₂+RO₂] and $j(\text{O}^1\text{D})$ or $\sqrt{j(\text{O}^1\text{D})}$ was found to be an unreliable indicator of net ozone production or destruction [*cf. Penkett et al., 1997; Monks et al., 1998; Zanis et al., 1999*], showing no significant relationship with N(O₃). In contrast, the rate of peroxide production was inversely correlated with ozone tendency; a similar effect was noted for EASE 97. The mixing ratios of NO required for photochemical balance of ozone (compensation point) were very similar to those obtained for EASE 97: 40±23 pptv using the peroxy radical mixing ratios as measured and 28±19 pptv using the peroxy radical measurements multiplied by two (the analogous EASE 97 values were 40±21 and 22±18 pptv, respectively). The ozone production efficiency with respect to NO_x oxidation (E_N) was in the range 10-50 at 150-450 pptv NO_x; very low or negative values were observed at lower NO_x, indicative of net ozone destruction. A positive correlation between ozone production efficiency and daytime ΔO₃ suggested that transport, as well as *in-situ* photochemistry, must be taken into account when considering E_N values [*cf. Rickard et al., 2001*].

The calculated contribution of formaldehyde photolysis to total HO_x production was significant in SOAPEX 2 (daytime mean 20% for baseline conditions), whereas peroxide photolysis was relatively unimportant (<10%). Total HO_x production rates were higher for non-baseline than baseline conditions (peak production rates *ca* 3.5×10⁶ molecules cm⁻³ s⁻¹ for baseline, 5.0×10⁶ molecules cm⁻³ s⁻¹ for non-baseline); this was largely due to higher humidities in non-baseline air, leading to higher OH production rates *via* reaction (5.31):



A similar difference in humidity between baseline and semi-polluted conditions was observed at Cape Grim during SOAPEX 1 [*Carpenter et al., 1997*]. Analogous rate of production analyses by wind sector for EASE 97 gave similar results, although a considerably higher mean contribution of formaldehyde photolysis to HO_x production was observed in the semi-polluted south-east wind sector (daytime mean 38%). OH loss was less dominated by CO and CH₄ than reported previously for EASE 96 [*Carslaw et al., 1999a*] and EASE 97 [*Carslaw et al., 2001a*]. This effect was largely explicable by the much lower CO mixing ratios at the Southern Hemisphere site (range of daytime means in data subsets 42-49 ppbv during SOAPEX 2; 98-165 ppbv at Mace Head during EASE 96/97). The mean contribution of CO to OH loss was 36% for baseline and 34% for non-baseline conditions.

NO_x lifetime analysis showed that the production rate of NO_x (P_{NO_x}) required to sustain the observed NO_x mixing ratios were just 1.0 and 8.5 pptv h^{-1} for SOAPEX 2 baseline and non-baseline conditions, respectively: considerably lower than for EASE 97 (wind sector means in range 15.1–101.2 pptv h^{-1}). The NO_x lifetimes during SOAPEX 2 were significantly longer than during EASE 97, particularly when τ_{NO} and τ_{NO_2} were considered singly.

The reaction of NO_3 and DMS was found to dominate night-time chemistry in baseline air, accounting for 97% of the total VOC oxidation, and was still significant in non-baseline conditions (59%). Such pre-eminence was not observed during EASE 97 (see Chapter 3), and was mainly caused by the much higher DMS mixing ratios observed at Cape Grim compared with Mace Head (baseline mean 85 pptv, compared to <20 pptv for all wind sectors in EASE 97). VOC oxidation excluding DMS was much higher in non-baseline conditions (5.9×10^3 molecules $\text{cm}^{-3} \text{s}^{-1}$ for baseline, 7.0×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$ for non-baseline conditions). Also in contrast with EASE 97 was the important contribution of NO_3 -alkene reactions to night-time alkene oxidation, particularly in baseline air (84%).

Peroxy radical production at night was also dominated by NO_3 reactions in baseline conditions (mean 89%), although the total production rate was very low compared with non-baseline conditions (mean value 6.0×10^3 molecules $\text{cm}^{-3} \text{s}^{-1}$). In non-baseline air, the NO_3 and O_3 oxidation mechanisms contributed approximately equally to peroxy radical production for most of the night, and peroxy radical production rates were comparable to those observed in EASE 97 (mean total 6.7×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$). The estimated rate of peroxy radical production in baseline air was 5 times lower than non-baseline air for the NO_3 mechanism, and 50 times lower for the O_3 mechanism.

Chapter 6 – Towards a Humidity Correction for the PERCA Instrument

6.1 Introduction

As discussed in Chapters 1 and 2, recently published work by *Mihele and Hastie* [1998] and *Mihele et al.* [1999] has established that the chain length (CLN) of a peroxy radical chemical-amplification instrument where the photolysis of water is used to generate HO_2 as a calibration source, is significantly reduced in humid air compared to the dry air value. A similar CLN-humidity effect has now been observed in laboratory experiments using the UEA-Leicester instrument (results presented in Chapter 2), where the calibration source for CLN determination is the photolysis of CH_3I in dry, synthetic air to yield CH_3O_2 radicals. The aim of this chapter is to examine whether the magnitude of the UEA-Leicester PERCA CLN reduction predicted by the laboratory measurements aids the interpretation of the field measurements obtained by the instrument since 1995, and particularly the results from the EASE 96, EASE 97 and SOAPEX 2 campaigns, where the PERCA inlet was maintained at above ambient temperatures (*ca* 30°C) in an effort to ameliorate the measurement deficit observed in earlier field campaigns [*Monks et al.*, 1998].

6.2 Calculated CLN-Humidity Effect for EASE 96, EASE 97 and SOAPEX 2

6.2.1 PERCA inlet temperature and ambient humidity during EASE 96, EASE 97 and SOAPEX 2

Figure 6.1 shows the PERCA instrument inlet temperature time series for SOAPEX 2, January-February 1999; over the whole campaign (day and night), the mean temperature recorded in the inlet unit was 30.3°C (standard deviation 2.7°C). Similar time series, with periods where the temperature dipped to *ca* 20°C and 'spikes' of higher temperatures (up to *ca* 45°C in the middle of sunny days), were obtained for the EASE campaigns (not shown). The mean inlet temperatures observed during all three campaigns are given in Table 6.1, as well as mean daytime (06:00-19:00) and night-time (19:00-06:00) values. The standard deviations for each mean (Table 6.1) show that the inlet temperature during EASE 97 was

somewhat more variable than during EASE 96 or SOAPEX 2; in general, the inlet temperature was also lower during the 1997 Mace Head campaign, with a prolonged period where the mean temperature was $<25^{\circ}\text{C}$ (days of year 125-128).

Figure 6.1 Time series of PERCA inlet temperature during SOAPEX 2, January-February 1999

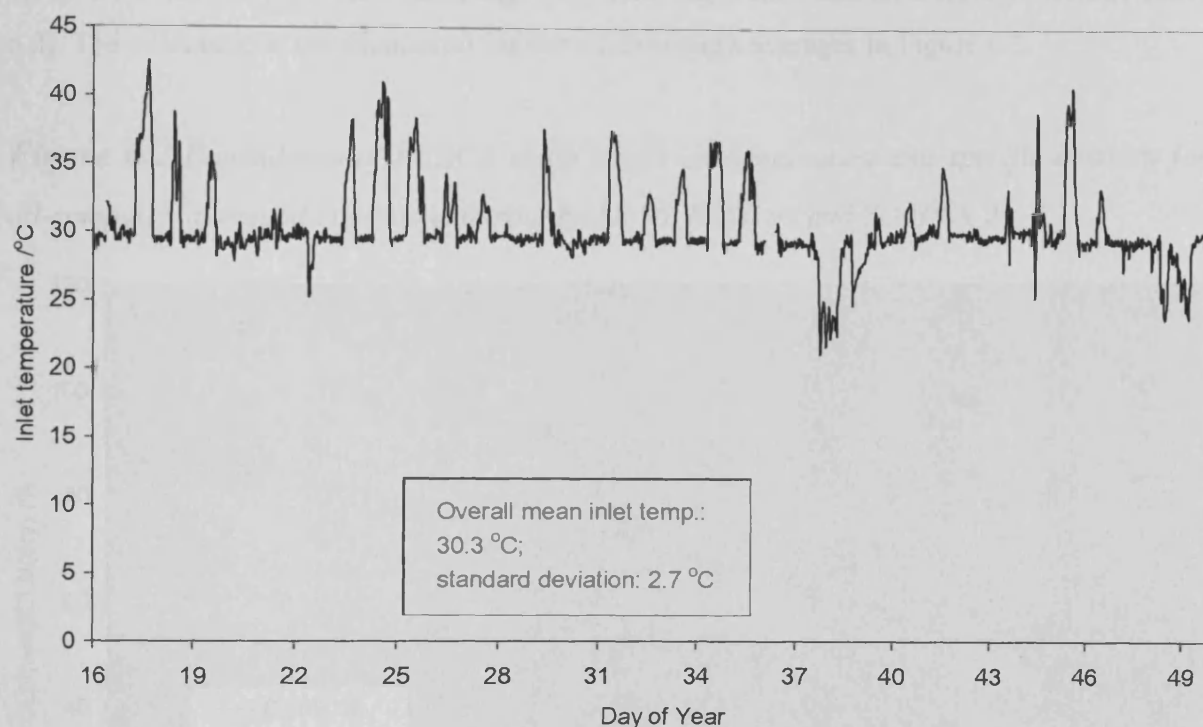


Table 6.1 PERCA inlet temperature and ambient specific humidity for averaged conditions during EASE 96, EASE 97 and SOAPEX 2

Quantity		EASE 96	EASE 97	SOAPEX 2
Temperature /°C	Daytime	32.0 (2.2)	28.3 (3.5)	31.2 (3.2)
	Night-time	31.0 (2.0)	26.3 (3.7)	29.2 (1.3)
	All	31.6 (2.2)	27.4 (3.7)	30.3 (2.7)
Specific humidity /g kg ⁻¹	Daytime	9.1 (0.0 ₅)	6.7 (0.1)	9.9 (0.1)
	Night-time	9.1 (0.1)	6.6 (0.1)	9.7 (0.1)
	All	9.1 (0.1)	6.7 (0.1)	9.8 (0.1 ₅)

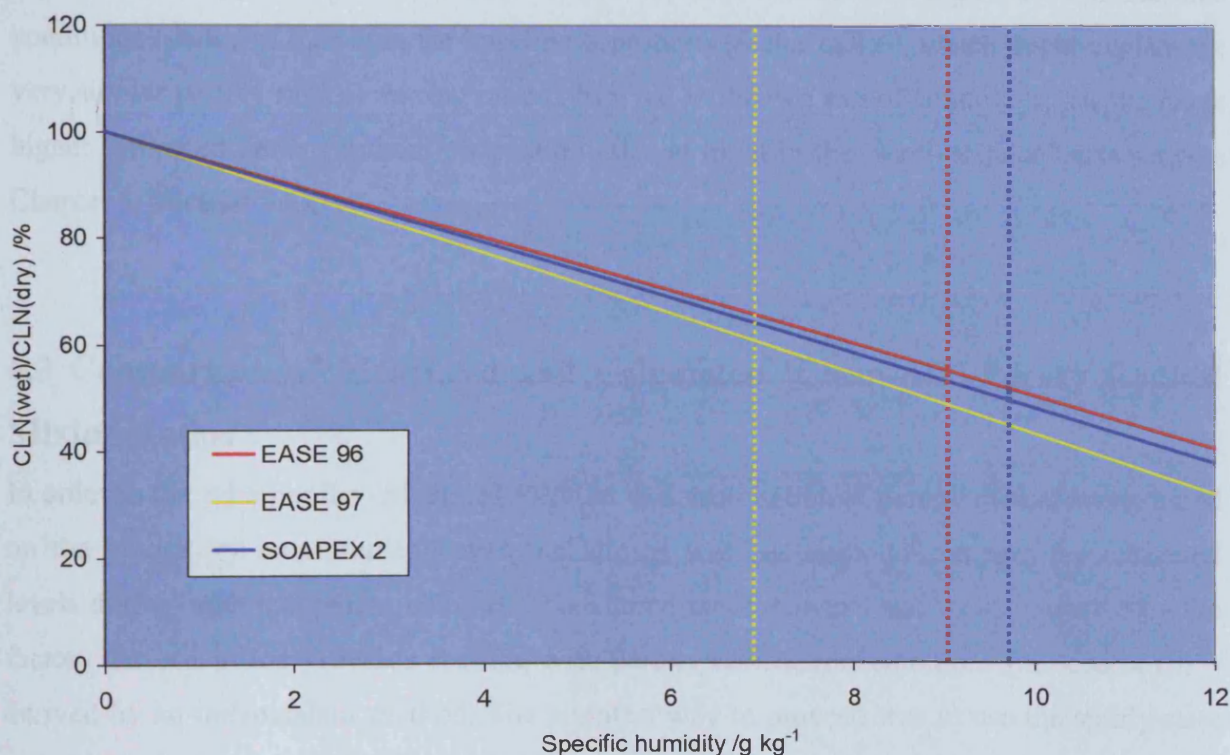
Also shown in Table 6.1 are the averaged ambient specific humidities observed in both the daytime and night-time periods for each campaign, as well as all-campaign averages. Once again, the EASE 97 value stands out slightly from the other two, with a campaign average

specific humidity of 6.7 g kg^{-1} , whereas the equivalent values for EASE 96 and SOAPEX 2 were both above 9 g kg^{-1} (9.1 and 9.8 g kg^{-1} , respectively).

6.2.2 Calculation of expected CLN reduction in humid air for each campaign

From the temperature dependence of the PERCA CLN-humidity effect observed in the laboratory experiments (Fig. 2.17), it was possible to calculate the expected CLN dependence on specific humidity for each campaign (daytime, night-time and all campaign means; Table 6.2). The calculations are illustrated for the all-campaign averages in Figure 6.2.

Figure 6.2 Dependence of PERCA chain length on temperature and specific humidity for all-campaign averaged conditions during EASE 96, EASE 97 and SOAPEX 2



The similar mean PERCA inlet temperatures and ambient humidities in EASE 96 and SOAPEX 2 (Table 6.1) were found to result in similar predicted CLN reductions (measurement *versus* dry, calibration mode) for the two campaigns (all-campaign means 45% and 51%, respectively). In contrast, the somewhat lower PERCA inlet temperatures and humidities during EASE 97 combined to give a somewhat lower CLN reduction (all-campaign mean 38%). It is also worth noting that there was little difference in the estimated CLN reduction in ambient, humid air between the daytime and night-time periods in any of the three campaigns (maximum difference 2%).

Table 6.2 Percentage reduction in PERCA chain length for each campaign based on average PERCA inlet temperatures and ambient specific humidities

CLN ('wet')/CLN('dry') /%	EASE 96	EASE 97	SOAPEX 2		
			Baseline	Non-baseline	All campaign
Daytime	55	63	62	46	50
Night-time	54	61	61	44	48
All	55	62	62	46	49

Since the measured peroxy radical mixing ratios derived from the PERCA instrument are proportional to $1/\text{CLN}$ (Chapter 2), the results in Table 6.2 imply that the campaign mean underestimation by the PERCA instrument was a factor of 1.8 ($1/0.55$) for EASE 96, 1.6 ($1/0.62$) for EASE 97, and 2.0 ($1/0.49$) for SOAPEX 2. The night-time results for SOAPEX 2 in Table 6.2 suggest that the PERCA underestimation was *ca* 40% higher for non-baseline conditions (factor of 2.2) than for baseline conditions (factor of 1.6), which might explain the very similar peroxy radical mixing ratios observed in the two sets of conditions, despite much higher estimated peroxy radical production rates at night in the 'semi-polluted' data set (see Chapter 5, Section 5.8).

6.3 Comparison of Measured and Calculated 'Clean-Air' Peroxy Radical Mixing Ratios

In order to see whether the calculated PERCA underestimation of peroxy radical levels based on the laboratory measurements was realistic, it was necessary to compare the measured levels during each campaign, using both unaltered measurements and those corrected by the factors derived in the previous section, with peroxy radical concentrations (molecules cm^{-3}) derived by an independent method. The simplest way to proceed was to use the steady-state expression derived by *Penkett et al.* [1997] to calculate peroxy radical levels in the zero- NO_x limit already introduced in Chapters 4 and 5:

$$[\text{HO}_2 + \text{RO}_2] = \left(\frac{f \cdot j(\text{O}^1\text{D}) \cdot [\text{O}_3]}{k'} \right)^{1/2} \quad (6.1)$$

where f is the fraction of singlet oxygen atoms that react with water, rather than undergoing collisional deactivation to ground-state oxygen atoms ($\text{O}(^3\text{P})$), and k' is a composite rate coefficient for the self- and cross-reactions of HO_2 and CH_3O_2 . (In Equation (6.1), CH_3O_2 is assumed to be the dominant organic peroxy radical present.) To calculate theoretical peroxy

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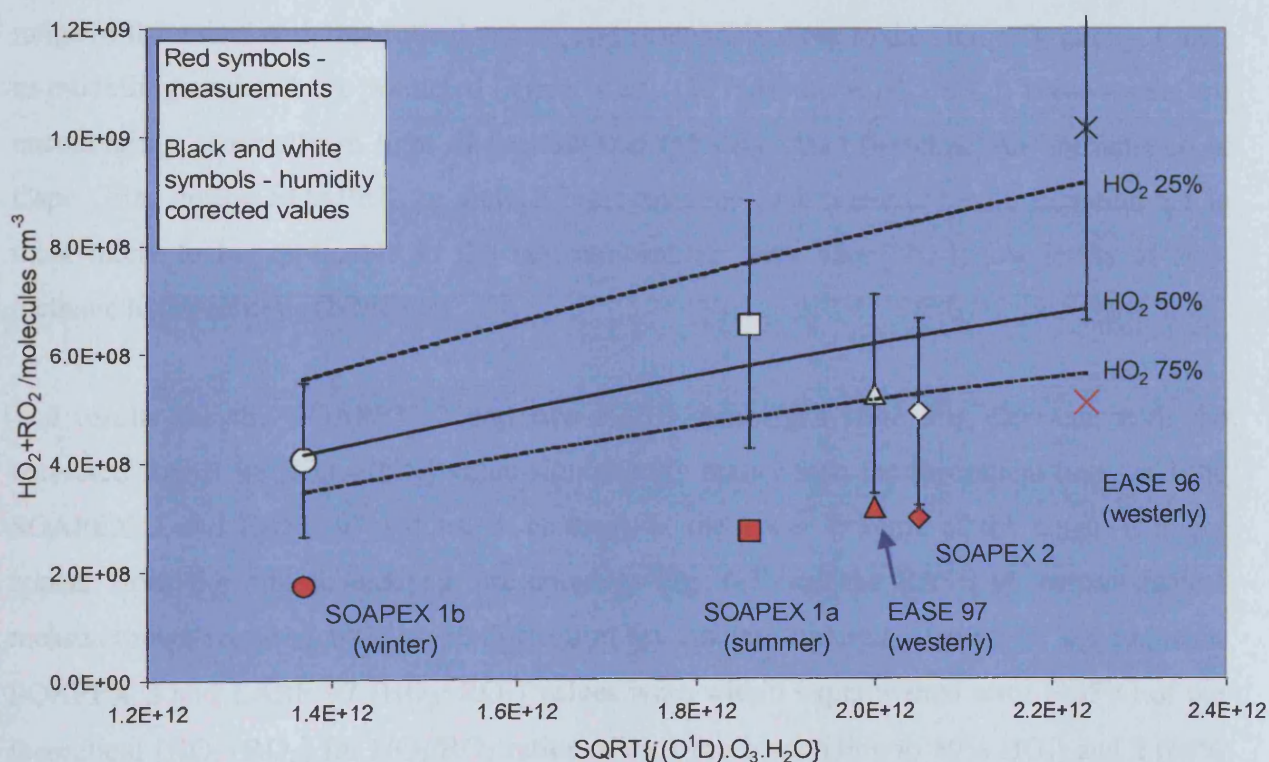
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radical concentrations from Equation (6.1), it is necessary to assume a value for the $\text{HO}_2/\text{CH}_3\text{O}_2$ ratio, which depends, amongst other factors, on the carbon monoxide and methane levels (see also Chapters 4 and 5). The procedure was adopted of calculating three sets of peroxy radical concentrations, using $\text{HO}_2/\text{CH}_3\text{O}_2$ ratios of 0.33, 1 and 3, in order to cover the likely range of this ratio for the atmospheric conditions at Mace Head [up to 2, see *Carslaw et al.*, 1999a] and Cape Grim [ca 0.7; see *Ayers et al.*, 1997; *Monks et al.*, 2000]. Figure 6.3 shows the theoretical midday (12:00-13:00 average) peroxy radical concentrations calculated for each campaign (plotted as smoothed lines) and each HO_2/RO_2 ratio (indicated as percentage HO_2 in Fig. 6.3) as a function of $\sqrt{j(\text{O}^1\text{D}) \cdot [\text{H}_2\text{O}] \cdot [\text{O}_3]}$. Clearly, the predicted peroxy radical levels rise as $\sqrt{j(\text{O}^1\text{D}) \cdot [\text{H}_2\text{O}] \cdot [\text{O}_3]}$ increases, as expected from Equation (6.1).

Figure 6.3 Measured and calculated 'clean-air' peroxy radical concentrations for the EASE and SOAPEX campaigns, with and without estimated humidity correction



Also plotted in Fig. 6.3 are the measured midday (12:00-13:00 average) peroxy radical concentrations from the two SOAPEX 1 campaigns (summer and winter; see Chapter 5), as well as from EASE 96, EASE 97 and SOAPEX 2 (all shown in red symbols). In each case, the 'cleanest' (lowest $[\text{NO}_x]$) subsets of the data were used, *i.e.*, the westerly sectors for EASE 96 and 97, and the baseline data sets (defined as in Chapter 5) for the three SOAPEX field deployments. The most striking thing about these results is that, for each campaign, the

measured levels fell substantially below the theoretical, calculated values (Equation 6.1). This observation is in qualitative agreement with the findings of *Monks et al.* [1998], described in detail in Chapter 5, where a systematic underestimation by a factor of *ca* 2 during SOAPEX 1a by the UEA-Leicester PERCA instrument was demonstrated by two independent criteria (Section 5.1.4).

The black and white symbols in Fig. 6.3 represent the results of applying the humidity corrections calculated in the last section to each midday average measurement value. The error bars represent $\pm 35\%$ on each $[\text{HO}_2 + \text{RO}_2]$ value (Chapter 2), and are omitted from the uncorrected measurements for the sake of clarity. For the SOAPEX 1 campaigns, where the PERCA inlet was unheated, and the temperature in the inlet unit was not monitored, the average daytime, ambient temperature was used to derive an approximate correction factor in each case (a factor of 2.4 for SOAPEX 1a and 2.3 for SOAPEX 1b). For the two SOAPEX 1 campaigns, Fig. 6.3 shows that the corrected peroxy radical concentrations were within the range of the calculated, theoretical values, and reasonably close to the HO_2/RO_2 ratio = 1 line, as modelling studies have predicted [*Ayers et al.*, 1997; *Monks et al.*, 2000]. These results are encouraging, especially in light of the fact that the very clean (baseline) air encountered at Cape Grim during SOAPEX 1a and 1b represents the case scenario where Equation 6.1 is most likely to be applicable in the real atmosphere: very low $[\text{NO}_x]$; low levels of non-methane hydrocarbons (NMHCs).

The results for the SOAPEX 2 and two EASE campaigns were less clear-cut, with the corrected EASE 96 $[\text{HO}_2 + \text{RO}_2]$ value significantly higher than the theoretical lines, and the SOAPEX 2 and EASE 97 values, in contrast, at the lower extreme of the range. It might appear from the simple analysis presented in Fig. 6.3 that the EASE 96 peroxy radical measurements required little or no correction for ambient humidity. However, the corrected SOAPEX 2 and EASE 97 $[\text{HO}_2 + \text{RO}_2]$ values were within experimental error ($\pm 35\%$) of the theoretical $[\text{HO}_2 + \text{RO}_2]$ for HO_2/RO_2 ratios of *ca* 1 (corresponding to 50% HO_2) and 2 (66% HO_2), respectively. It is also worth noting that the SOAPEX 2 baseline data set was small compared with those obtained in the 1995 campaigns (see Chapter 5).

The contradictory results obtained for the EASE campaigns possibly reflect the fact that Equation (6.1) might not be applicable to the conditions encountered at Mace Head, where significant NO_x is present even in the cleanest air masses (see Chapter 4), and organic peroxy

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The contradictory results obtained for the EASE campaigns possibly reflect the fact that Equation (6.1) might not be applicable to the conditions encountered at Mace Head, where significant NO_x is present even in the cleanest air masses (see Chapter 4), and organic peroxy

radicals other than CH_3O_2 are likely to be present at appreciable mixing ratios [Carslaw *et al.*, 1999a].

6.4 Comparison of Measured Peroxy Radicals during EASE 96 and EASE 97 with Box Model Results

6.4.1 Comparison method

Since the PERCA technique has less than 100% detection efficiency for each peroxy radical [Ashbourn *et al.*, 1998], it is conventional to take the sensitivities of the measurement technique to each species into account when comparing modelled to measured concentrations [Carslaw *et al.*, 1999a, 2001a]. However, since the UEA-Leicester chain length determinations already consider the fact that the conversion of CH_3O_2 into HO_2 , and hence its detection efficiency, is only *ca* 80% (Chapter 2, Equation 2.2), it might be thought erroneous to make further allowance for <100% detection of all peroxy radicals, since most of the relatively small (and generally most atmospherically abundant) peroxy radicals have similar detection efficiencies in the range 70-80% [Ashbourn *et al.*, 1998]. A short thought experiment is offered to show that this is not the case.

Suppose, first, that the PERCA calibration source produces 50 pptv [CH_3O_2]; the apparent chain length (CLN) is given by

$$\text{CLN} = \Delta\text{NO}_2 / [\text{CH}_3\text{O}_2] \quad (6.2)$$

This *ignores* the 80% detection efficiency of CH_3O_2 . If a calibration is performed, and ΔNO_2 is 4 ppbv, it follows that the chain length is given by $\text{CLN} = 4000/50 = 80$. Turning now to atmospheric measurements, suppose that on a particular day during a field campaign the real midday maximum [$\text{HO}_2 + \text{RO}_2$] is 25 pptv. To a first approximation, if the main peroxy radicals present are HO_2 and CH_3O_2 , the sensitivity of the PERCA is still *ca* 80% for the real atmosphere [Ashbourn *et al.*, 1998], so the PERCA signal observed will be 2 ppbv ΔNO_2 : nothing has changed between calibration mode and measurement mode, if the humidity effect is neglected. In this scenario, the PERCA instrument measures $2000/80$ or 25 pptv [$\text{HO}_2 + \text{RO}_2$]: the correct result. In practice, however, the apparent chain length is corrected by a factor of 0.85, to allow for the detection efficiency of CH_3O_2 :

$$\text{CLN} = \Delta\text{NO}_2 / (0.85 * [\text{CH}_3\text{O}_2]) \quad (6.3)$$

so that a CLN of $4000 / (0.85 * 50) = \text{ca } 94$ is obtained. In this case, when it comes to the midday measurement, 2 ppbv ΔNO_2 is still observed, but $[\text{HO}_2 + \text{RO}_2]$ is calculated to be $2000/94 = 21.3$ pptv.

It follows, therefore, that the observed peroxy radical mixing ratios must be corrected by the factor of *ca* 0.8 again. In fact, if the apparent CLN in calibration mode were not corrected, there would be no need to make the correction again when comparing modelled to measured peroxy radical mixing ratios. It must be stressed again, however, that this argument relies on the fact that the PERCA detection efficiency of all significant peroxy radicals is similar to that of CH_3O_2 .

The EASE peroxy radical measurements were compared with the outputs from two different modelling studies; introductions to the models used and the results of each comparison are given in the following sections.

6.4.2 The University of Leeds generic box model[†]

The campaign-tailored box models developed at the University of Leeds used to predict $[\text{OH}]$, $[\text{HO}_2]$ and $[\text{RO}_2]$ during EASE 96 and EASE 97 have been described in detail previously [Carslaw *et al.*, 1999a, b; 2001a,b; Jacobs, 2000]. Since these radical species have short lifetimes, their concentrations react rapidly to changes in local conditions, such as solar flux, but are not affected by transport. To a first approximation, therefore, it is possible to use a model containing no spatial information (*zero-dimensional model*) to describe the behaviour of OH and peroxy radicals, given a knowledge of the concentrations of sufficient trace species measured concurrently (and therefore in the same air mass). Indeed, for each of the EASE campaigns, the University of Leeds box model was constrained by observations of NO, NO₂, O₃, H₂, CO, CH₄, NMHCs, HCHO, PAN, SO₂, aerosol surface area, $j(\text{O}^1\text{D})$, $j(\text{NO}_2)$, temperature and water vapour mixing ratio, all averaged to 15 min model input points. The model also included dry deposition and heterogeneous loss terms, as described by Carslaw *et al.* [1999a]. With the exception of the DMS mechanism from Yin *et al.* [1990a, b], the chemical mechanisms and rate coefficients for all species were taken from a Master Chemical Mechanism (MCM) devised by Jenkin *et al.* [1997]. In total, 1666 reactions and 505 species

[†] The University of Leeds model data were kindly supplied by Dr Nicola Carslaw, now at the University of York, and Dr Phil Jacobs.

for EASE 96 [Carslaw et al., 1999b], and 1646 reactions and 488 species for EASE 97 [Carslaw et al., 2001a] were included. The model uncertainties in $[\text{HO}_2 + \Sigma \text{RO}_2]$ were estimated to be 25-27% (2σ), depending on the atmospheric conditions [Carslaw et al., 1999a, 2001a]. The FACSIMILE numerical integration package [AEA Technology, 1995] was employed for both sets of simulations (see Chapter 2 for more details).

6.4.3 Results of the Leeds-model/measurement comparison

Carslaw et al. [1999a, 2001a] have shown previously that the level of qualitative agreement between the PERCA measurements and the Leeds modelled $[\text{HO}_2 + \text{RO}_2]$ during EASE 96 and EASE 97 was generally good, with short timescale variations in measured $[\text{HO}_2 + \text{RO}_2]$ (caused by passing cloud reducing the local solar flux, for example) often well reproduced by the model output. In contrast, the purpose of this section is to look at overall mean ratios of modelled/measured $[\text{HO}_2 + \text{RO}_2]$, in order to see what the impact of the possible PERCA humidity correction would be on the level of agreement between model and measurement. To this end, mean hourly model/measurement $[\text{HO}_2 + \text{RO}_2]$ ratios were calculated using the Leeds air mass classifications for each campaign described in Section 4.2.2 of Chapter 4. To see if the daytime and night-time levels of agreement were different, data were further divided into broad daytime (06:00-19:00) and night-time (19:00-06:00) periods in each case. The results of this analysis are presented in Tables 6.3 (a) for EASE 96, and (b) for EASE 97.

Table 6.3 Daytime (06:00-19:00) and night-time (19:00-06:00) Leeds-modelled/measured $[\text{HO}_2 + \text{RO}_2]$ ratios by air mass during EASE 96 and EASE 97

(a) EASE 96^a

Period	Anticyclonic (UK semi-polluted)		Westerly	
	17 th July	18 th July	2 nd August	3 rd August
Daytime	2.15 (1.02)	1.88 (2.15)	0.75 (0.61)	1.03 (1.00)
Night-time	2.00 (0.94)	1.41 (1.12)	0.89 (1.43)	1.21 (1.85)

(b) EASE 97^a

Period	UK	France	Polar
Daytime	0.91 (0.72)	1.50 (1.28)	1.62 (0.80)
Night-time	0.77 (0.36)	0.76 (0.47)	0.64 (0.38)

^a Figures in brackets are standard deviations of the modelled/measured $[\text{HO}_2 + \text{RO}_2]$ for each data subset.

First, it is important to recognise the degree of variability in the modelled/measured $[\text{HO}_2 + \text{RO}_2]$ ratios, where the standard deviation for each set of conditions in both campaigns was often a large percentage of the average value (over 100% in some cases). In addition, Table 6.3 (a) shows that, for the four days modelled during EASE 96, the daytime and night-time modelled/measured $[\text{HO}_2 + \text{RO}_2]$ ratios were quite similar for both semi-polluted and clean air masses. However, the actual ratios obtained were significantly different in the two sets of conditions, with an average $[\text{HO}_2 + \text{RO}_2]$ ratio range of 1.41-2.15 for semi-polluted air, compared to a range of 0.75-1.21 for clean air off the mid-Atlantic. Examination of the PERCA temperature and ambient humidity data for these four days gave an expected mean underestimation factor in the PERCA measurements (calculated based on the laboratory characterisation experiments, as described in Section 6.2) of 1.6 (daytime) and 1.7 (night-time) for 17th-18th July and 1.7 (daytime) and 1.8 (night-time) for 2nd-3rd August. The conclusion from this work for EASE 96 must be, therefore, that the level of quantitative agreement for the semi-polluted days is approximately in the range expected based on the PERCA CLN reduction in humid air, given the uncertainties in both model (*ca* 25%) and measurements (*ca* 35%), whereas for the relatively clean days, the level of quantitative agreement is rather better than would be expected. The reasons for this difference between the two sets of conditions remain unclear (see Section 6.4.5).

Table 6.3 (b) shows the analogous ratios for the EASE 97 campaign, where three distinct periods were modelled by the University of Leeds (see Chapter 4). In each case, the modelled/measured $[\text{HO}_2 + \text{RO}_2]$ ratio was higher during the daytime than at night; this is puzzling, since no such clear distinction was seen in the EASE 96 data set. The daytime modelled/measured $[\text{HO}_2 + \text{RO}_2]$ ratio was *ca* 1.5-1.6 for two of the air masses (*France*, semi-polluted; *Polar*, relatively clean), in good agreement with the expected underestimation factor based on campaign-averaged PERCA inlet temperature and ambient humidity (1.6; Section 6.2). Nevertheless, once more a set of conditions was encountered where the level of quantitative agreement between modelled and measured $[\text{HO}_2 + \text{RO}_2]$ was better than expected: this time, however, it was in semi-polluted air (*UK* air mass), where the mean $[\text{HO}_2 + \text{RO}_2]$ ratio was 0.91.[†] Table 6.4 shows the average daytime/night-time PERCA inlet temperature, ambient specific humidity and expected PERCA measurement underestimation for each of the three periods during EASE 97 where modelled data were available.

[†] These results are similar to those calculated for the 11:00-15:00 daytime period only by Carslaw *et al.* [2001a]: France 1.4; Polar 1.6; UK 1.0.

Table 6.4 PERCA inlet temperature, ambient specific humidity and expected PERCA measurement underestimation based on laboratory work for each of the three EASE 97 campaign periods modelled by the University of Leeds

Quantity	UK		France		Polar	
	(Days of year 136-145)		(Days of year 120-123)		(Days of year 125-135)	
	Daytime	Night-time	Daytime	Night-time	Daytime	Night-time
Specific humidity /g kg ⁻¹	7.4	7.2	7.9	7.5	5.5	5.6
PERCA inlet temperature /°C	30.2	28.3	30.4	28.9	25.5	22.9
Expected PERCA underestimation factor	1.6	1.7	1.7	1.7	1.5	1.6

Table 6.4 shows that, although the polar period was characterised by lower PERCA inlet temperatures than either the UK or France periods, lower ambient humidity levels were also observed during this part of the campaign. These two effects tended to counterbalance each other, leading to a similar expected PERCA measurement underestimation due to the CLN-humidity effect for each of the three periods (range 1.5-1.7). It is also worth noting from Table 6.4 that little difference in PERCA performance would be expected between daytime and night-time periods. In conclusion, therefore, the better agreement between modelled and measured [HO₂+RO₂] in the UK period than during the France or Polar periods during EASE 97 cannot be explained simply by reference to the PERCA CLN-humidity effect.

6.4.4 The University of East Anglia (UEA) modelling study of radical chemistry during EASE 96[†]

A second zero-dimensional box model was used to investigate selected periods during EASE 96 (see Table 6.5), based on a model used previously in a number of published studies [*e.g.*, *Derwent et al.*, 1996; *Grenfell et al.*, 1999b]. For the runs used in this comparison, the UEA model was constrained by measurements of NO, NO₂, O₃, CO, CH₄, NMHCs, *j*(O¹D), *j*(NO₂), temperature and dew point, all averaged to 15 min model input points. Model runs were also initialised with set mixing ratios of H₂O₂, HNO₃, HONO, HCHO, H₂ and PAN, based on measurements where available, or estimated otherwise. The chemical mechanism used in the UEA model was based on that of *Derwent et al.* [1996], and included 1284 reactions and 602 species; dry deposition and heterogeneous loss terms were also included. The FACSIMILE

[†] The UEA model data were kindly supplied by Mr Richard Crowther, now at the University of Cambridge.

numerical integration package [AEA Technology, 1995] was employed for the UEA modelling study, as described previously. Full details of the UEA model developed for EASE 96 may be found in Crowther [2001].

Table 6.5 Daytime (06:00-19:00) and night-time (19:00-06:00) UEA-modelled/measured $[HO_2+RO_2]$ ratios by air mass during EASE 96

Period	UK (anti-cyclonic) semi-polluted: 16th-18 th July	Mid-latitude maritime: 2 nd -4 th August
Daytime	2.28 (1.32)	0.71 (0.61)
Night-time	1.38 (1.59)	0.40 (0.32)

The two UEA-modelled periods roughly corresponded to the periods modelled by the University of Leeds (Table 6.3 (a)). Comparison of the results in Tables 6.3 (a) and 6.5 shows that similar modelled/measured $[HO_2+RO_2]$ ratios were obtained from the two model comparisons, although there was more contrast between daytime and night-time in the UEA mean ratios. Once again, the standard deviations in Table 6.5 show that the modelled/measured ratios were highly variable. In addition, a similar contrast in levels of absolute agreement in peroxy radical mixing ratios between semi-polluted and clean-air conditions was observed in the UEA model/measurement comparison as noted previously for the Leeds model/measurement comparison (Section 6.4.3). No explanation of this contrast could be obtained by consideration of the expected PERCA underestimation due to the CLN-humidity effect for the two sets of conditions: for the 16th-18th July, the expected underestimation factors based on the lab experiments were 1.6 (daytime) and 1.7 (night-time); for the period 2nd-4th August, the expected underestimation factors were 1.7 (daytime) and 1.8 (night-time), *i.e.*, not significantly different.

6.4.5 Discussion of the model/measurement comparisons

Leaving aside for a moment the PERCA CLN-humidity effect, other possible reasons for the differing levels of agreement between modelled and measured $[HO_2+RO_2]$ in different conditions include peroxy radical speciation and shortcomings in the constraining data set and/or reaction schemes of the box models. In relatively polluted air, where the VOC loading is high and the mix of VOCs complex, a wide variety of peroxy radicals are likely to be present, some of which may not be detected efficiently by the PERCA technique [Ashbourn *et al.*, 1998]. Equally, some limitations in the modelling of relatively polluted air masses are probable owing to both the lack of higher molecular mass VOC measurements and accurate laboratory kinetic data for a sufficient range of reactions. Neither of these problems seems

likely to pertain to relatively clean air; it might also be noted that the two effects will tend to counterbalance each other in model/measurement $[\text{HO}_2+\text{RO}_2]$ comparisons for polluted air.

To summarise briefly the last two sections, both the Leeds and UEA box model/measurement comparisons for EASE 96 gave modelled/measured $[\text{HO}_2+\text{RO}_2]$ ratios roughly in line with those expected on the basis of the laboratory measured PERCA CLN-humidity effect in the UK polluted air mass, with closer agreement than expected in the clean, maritime air mass. Conversely, for EASE 97, both the relatively clean Polar air mass and the polluted France air mass gave modelled/measured $[\text{HO}_2+\text{RO}_2]$ ratios roughly as expected, whereas the UK air mass agreement was better than expected. There were also significant differences between the levels of agreement observed in the daytime and night-time periods in EASE 97; such an effect was not noted for EASE 96. In conclusion, there was no simple relationship between model/measurement ratio and the nature of the air mass, which might suggest that neither peroxy radical speciation nor shortcomings in the box model reaction schemes were straightforwardly responsible for better than expected model/measurement agreement in some air masses. As noted previously, the model/measurement ratios were highly variable in all air masses, and it might be that the combined model/measurement error could account for some of the apparent discrepancies described here.

6.5 Summary and Conclusions

From the temperature dependence of the PERCA CLN-humidity effect observed in the laboratory experiments (Chapter 2), the expected CLN dependences on specific humidity for EASE 96, EASE 97 and SOAPEX 2 were calculated, based on the mean PERCA inlet temperature and mean ambient specific humidity for each campaign (daytime, night-time and all-campaign averages). Similar calculations were carried out for the SOAPEX 1a and 1b campaigns, based on ambient temperature measurements. The campaign mean PERCA underestimation factors were calculated to be 2.4 for SOAPEX 1a, 2.3 for SOAPEX 1b, 1.8 for EASE 96, 1.6 for EASE 97 and 2.0 for SOAPEX 2. These factors were used to compare the average midday (12:00-13:00) $[\text{HO}_2+\text{RO}_2]$ measurements, with and without the putative humidity correction, with calculated values based on the low NO_x , steady-state expression derived by *Penkett et al.* [1997]. For the two SOAPEX 1 campaigns, the corrected peroxy radical concentrations were within the range of the calculated, theoretical values, and reasonably close to the HO_2/RO_2 ratio = 1 line, as modelling studies have predicted [*Ayers et al.*, 1997; *Monks et al.*, 2000]. The results for the SOAPEX 2 and two EASE campaigns were

less clear-cut, with the corrected EASE 96 $[\text{HO}_2+\text{RO}_2]$ value significantly higher than the theoretical lines, and the SOAPEX 2 and EASE 97 values, in contrast, at the lower extreme of the range, although the latter two results were within experimental error ($\pm 35\%$) of the theoretical $[\text{HO}_2+\text{RO}_2]$ for HO_2/RO_2 ratios of *ca* 1 (corresponding to 50% HO_2) and 2 (66% HO_2), respectively. It is also worth noting that the SOAPEX 2 baseline data set was small compared with those obtained in the 1995 campaigns (Chapter 5).

The peroxy radical measurements during EASE 96 and EASE 97 were compared with the results of two box modelling studies by the University of Leeds (both campaigns) and the University of East Anglia (UEA; EASE 96 only). Both the Leeds and UEA model/measurement comparisons for EASE 96 gave modelled/measured $[\text{HO}_2+\text{RO}_2]$ ratios roughly in line with those expected on the basis of the laboratory measured PERCA CLN-humidity effect in the UK polluted air mass, with closer agreement than expected in the clean, maritime air mass. Conversely, for EASE 97, both the relatively clean Polar air mass and the polluted France air mass gave modelled/measured $[\text{HO}_2+\text{RO}_2]$ ratios roughly as expected, whereas the UK air mass agreement was better than expected. There was no simple relationship between model/measurement ratio and the nature of the air mass, which might suggest that neither peroxy radical speciation nor shortcomings in the box model reaction schemes were responsible for better than expected model/measurement agreement in some air masses, bearing in mind the likely PERCA underestimation factors calculated for each set of conditions.

In conclusion, it cannot be claimed that the PERCA CLN-humidity effect accounted well for different levels of agreement noted in the model/measurement comparisons over the whole range of pollution regimes encountered in the EASE campaigns. However, the model/measurement ratios were highly variable in all air masses, and it is likely that the combined model/measurement errors could account for some of the apparent discrepancies described here. The fact that the application of the low- NO_x steady-state expression (Equation 6.1) and the humidity correction for midday $[\text{HO}_2+\text{RO}_2]$ worked well for the SOAPEX 1 campaigns (Fig. 6.3) was encouraging, since the very clean air encountered at Cape Grim during SOAPEX 1a and 1b (classified as baseline by the original CSIRO criteria, see Chapter 5, Section 5.1.3) represents the case scenario where Equation (6.1) is most likely to be applicable in the real atmosphere: very low $[\text{NO}_x]$; low levels of non-methane hydrocarbons (NMHCs).

Chapter 7 – Conclusions and Suggestions for Further Research

7.1 Conclusions

7.1.1 Introduction

The aim of this short chapter is to bring together the main conclusions from Chapters 2-6, and draw comparisons where applicable. In the course of this work, research into the chemistry of peroxy radicals in the marine boundary layer has been undertaken in three broad areas. The first of these comprised an investigation into the accuracy of peroxy radical measurements using the chemical amplification technique in the humid atmosphere, and focused on characterisation of the performance of the UEA-Leicester PERCA instrument as a function of temperature and humidity (see Section 7.1.2).

The second aim of the project was to investigate *in-situ* ozone photochemistry at two contrasting measurement sites during three intensive field campaigns: two at Mace Head, on the Atlantic coast of Ireland in summer 1996 (EASE 96) and spring 1997 (EASE 97), and one at Cape Grim, on the north-west tip of Tasmania, Australia, in Austral summer 1999 (SOAPEX 2). The major conclusions from this work are given in Section 7.1.3.

The third distinct area of research concerned the oxidation of volatile organic compounds (VOCs) at night, and consequently the night-time formation of peroxy radicals during the EASE 97 and SOAPEX 2 campaigns; the results of this work are summarised in Section 7.1.4.

7.1.2 Characterisation of the PERCA instrument in humid air

A series of laboratory experiments with the UEA-Leicester PERCA instrument showed that the chain length (CLN) of the inlet amplification reaction decreased markedly with increasing specific humidity, in qualitative agreement with the previously published results of *Mihele and Hastie* [1998] and *Mihele et al.* [1999]. The magnitude of the PERCA CLN-humidity effect was reduced by warming the inlet. A qualitatively different temperature dependence was observed in a set of experiments where the glass inlet surface was coated with

polyphosphoric acid, although a standard statistical test showed no significant difference between the two data sets. Modelling of the PERCA inlet chemistry using the measured CLN(wet)/CLN(dry) ratios for given temperature and humidity gave fitted HO₂ wall-loss rate coefficients in good agreement with those measured experimentally by *Mihele et al.* [1999], which would suggest that enhanced wall losses of HO₂ in humid air are sufficient to explain the observed CLN-humidity effect.

From the laboratory measurements, the campaign mean PERCA underestimation factors were calculated to be 2.4 for SOAPEX 1a[†], 2.3 for SOAPEX 1b, 1.8 for EASE 96, 1.6 for EASE 97 and 2.0 for SOAPEX 2, based on mean PERCA inlet temperatures and ambient humidities for each campaign. These factors were used to compare the average midday (12:00-13:00) [HO₂+RO₂] measurements, with and without the putative humidity correction, with calculated values based on the low NO_x steady-state expression for [HO₂+RO₂] derived by *Penkett et al.* [1997]:

$$[\text{HO}_2 + \text{RO}_2] = \left(\frac{f \cdot j(\text{O}^1\text{D}) \cdot [\text{O}_3]}{k'} \right)^{1/2} \quad (7.1)$$

For the two SOAPEX 1 campaigns, the corrected peroxy radical concentrations were within the range of the calculated, theoretical values, and reasonably close to the HO₂/RO₂ ratio = 1 line, as modelling studies have predicted [*Ayers et al.*, 1997; *Monks et al.*, 2000]. The results for the SOAPEX 2 and two EASE campaigns were less clear-cut, with the corrected EASE 96 [HO₂+RO₂] value significantly higher than the theoretical lines, and the SOAPEX 2 and EASE 97 values, in contrast, at the lower extreme of the range, although the latter two results were within experimental error (±35%) of the theoretical [HO₂+RO₂] for HO₂/RO₂ ratios of *ca* 1 (corresponding to 50% HO₂) and 2 (66% HO₂), respectively.

A comparison between the peroxy radical measurements during EASE 96 and EASE 97 and the outputs of two box modelling studies by the University of Leeds (both campaigns) and the University of East Anglia (UEA; EASE 96 only) gave mixed results. In some air masses, the model/measurement ratio was similar to that expected based on the PERCA humidity correction factor estimated from the laboratory measurements. In others, notably a relatively clean, maritime air mass (*Westerly*) during EASE 96 and a polluted air mass (*UK*) during

[†] This factor may be compared with those derived by *Monks et al.* [1998] of 1.7 and 2.2, using two independent criteria (see Chapter 5, Section 5.1.4).

EASE 97, agreement between model and measurement was rather better than expected. As there was no clear relationship between model/measurement ratio and the nature of the air mass, it might be suggested that neither peroxy radical speciation nor shortcomings in the box model reaction schemes were responsible for better than expected model/measurement agreement in some air masses.

In conclusion, it cannot be claimed that the PERCA CLN-humidity effect accounted well for different levels of agreement noted in the model/measurement comparisons over the whole range of pollution regimes encountered in the EASE campaigns. However, the model/measurement ratios were highly variable in all air masses, and it is likely that the combined model/measurement errors could account for some of the apparent discrepancies. The fact that the application of the low- NO_x steady-state expression and the humidity correction for midday $[\text{HO}_2 + \text{RO}_2]$ worked well for the SOAPEX 1 campaigns (see Chapter 6, Fig. 6.3) was encouraging, since the very clean air encountered at Cape Grim during SOAPEX 1a and 1b (classified as baseline by the original CSIRO criteria, see Chapter 5, Section 5.1.3) represents the case scenario where Equation (7.1) is most likely to be applicable in the real atmosphere: very low $[\text{NO}_x]$; low levels of non-methane hydrocarbons (NMHCs).

7.1.3 Ozone photochemistry at Mace Head and Cape Grim

Analysis of photochemical ozone tendency by wind sector during the EASE campaigns showed that the overall ozone production at Mace Head was dominated by polluted air masses originating in Britain and continental Europe for both summer 1996 and spring 1997 (SE wind sector). The proportion of such polluted air masses encountered at Mace Head was much greater in spring than in summer; in addition, the ozone tendency was greater for each wind sector in the spring campaign than in the summer campaign, owing to higher levels of all measured pollution tracers in spring 1997 than in summer 1996. These two factors combined to ensure that the average ozone production rate was two times higher for spring 1997 than for summer 1996: $0.5^{+0.3}_{-0.2}$ ppbv h^{-1} for EASE 96, $1.0^{+0.5}_{-0.3}$ ppbv h^{-1} for EASE 97. The error limits are estimates based on the instrumental uncertainties of the PERCA $[\text{HO}_2 + \text{RO}_2]$ and radiometric $j(\text{O}^1\text{D})$ measurements, and allow for the likely magnitude of the humidity effect on the PERCA measurements (see Section 7.1.2). The averaged ozone production rates show the importance of urban plumes to the ozone budget of even remote locations in the Northern Hemisphere, and strongly suggest that the Northern Hemisphere spring ozone maximum is controlled, at least in part, by *in-situ* photochemistry [Monks, 2000].

In contrast, ozone tendency calculations for SOAPEX 2 showed that daytime ozone production and destruction were finely balanced for much of the campaign, whether the peroxy radical mixing ratios were used as measured or multiplied by a factor of two; little difference was observed between clean-air (baseline) and 'semi-polluted' (non-baseline) conditions (daytime mean $N(O_3)$ values -0.12 and -0.06 ppbv h^{-1} , respectively). The contrast between Mace Head and Cape Grim is perhaps not surprising, given that NO mixing ratios in 'semi-polluted' conditions at the Southern Hemisphere site were generally as low as, if not lower than those in the cleanest conditions experienced at Mace Head (W wind sector); see Chapter 5, Table 5.7. However, the mixing ratios of NO required for photochemical balance of ozone (compensation point) were very similar to those obtained for EASE 97: 40 ± 23 pptv using the peroxy radical mixing ratios as measured and 28 ± 19 pptv using the peroxy radical measurements multiplied by two (the analogous EASE 97 values were 40 ± 21 and 22 ± 18 pptv, respectively), although the large error limits on these values show the difficulty of estimating the compensation point with precision.

The calculated contribution of formaldehyde photolysis to total HO_x production was significant in both EASE 97 (e.g., 25% for the W wind sector) and SOAPEX 2 (20% for baseline conditions), whereas peroxide photolysis was relatively unimportant (<10% in all data sub-sets). The highest mean contribution of formaldehyde photolysis to HO_x production was observed in the semi-polluted SE wind sector during EASE 97 (daytime mean 38%). OH loss during SOAPEX 2 was less dominated by CO and CH_4 than reported previously for EASE 96 [Carslaw *et al.*, 1999a] and EASE 97 [Carslaw *et al.*, 2001a]: this effect was largely explicable by the much lower CO mixing ratios at the Southern Hemisphere site (range of daytime means in data subsets 42-49 ppbv during SOAPEX 2; 98-165 ppbv at Mace Head during EASE 96/97). No strong differences in the relative contributions of different species to HO_x production or OH loss rates were observed between baseline and non-baseline conditions in SOAPEX 2.

The general lack of differentiation between daytime baseline and non-baseline conditions during SOAPEX 2 may reflect the fact that very few periods of baseline air meeting the strict definition used by the CSIRO [e.g., Galbally *et al.*, 2000] were encountered during the campaign. Although pollution tracer levels were generally very low, therefore, in comparison with even a remote site such as Mace Head in the Northern Hemisphere, they were probably still not representative of air masses untouched by human influence for several weeks or

more, the sampling of which was the primary purpose of the field campaign at Cape Grim in Austral summer 1999.

7.1.4 Night-time chemistry at Mace Head and Cape Grim

The sustained mixing ratios of peroxy radicals observed at night at Mace Head during EASE 97 (net decay rates of <0.5 pptv h⁻¹ in all wind sectors) demonstrated a requirement for substantial radical production processes, in the absence of daytime photochemistry. In support of this finding, the average modelled lifetimes of HO₂ and RO₂ (where CH₃O₂ was taken to represent all RO₂ present) were all less than 1 h and 3 h, respectively, even with [NO] set to zero. The ozone-initiated oxidation routes of VOCs outweighed those of NO₃ in the NW, NE and SE wind sectors; in the SW sector the two mechanisms operated at similar rates on average, and oxidation by NO₃ was the dominant route in the W sector. The oxidation of alkenes at night by ozone was greater by a factor of four than that by NO₃ over the whole EASE '97 data set. Peroxy radical rate of production analyses showed that ozone reactions produced more peroxy radicals over the whole night-time period (defined as where [NO₃] $\neq 0$) than nitrate reactions (66 *versus* 34%, on average). However, the two mechanisms were found to operate at a similar rate in the middle of the night, when [NO₃] was highest. The main importance of these results is perhaps that there was a significant contribution from both the O₃ and NO₃ oxidation mechanisms, since previous studies have tended to emphasise one as dominant over the other.

During SOAPEX 2, the reaction of NO₃ and DMS was found to dominate night-time chemistry in baseline air, accounting for 97% of the total VOC oxidation, and was still significant in non-baseline conditions (59%). Such pre-eminence was not observed at night during EASE 97, and was mainly caused by the much higher DMS mixing ratios observed at Cape Grim compared with Mace Head (baseline mean 85 pptv, compared to <20 pptv for all wind sectors in EASE 97). VOC oxidation excluding DMS was much higher in non-baseline conditions (5.9×10^3 molecules cm⁻³ s⁻¹ for baseline, 7.0×10^4 molecules cm⁻³ s⁻¹ for non-baseline conditions), and comparable with the rates observed in EASE 97 (for example, 6.8×10^4 molecules cm⁻³ s⁻¹ for the SW wind sector). The contribution of NO₃-alkene reactions to night-time alkene oxidation was much more significant at Cape Grim than at Mace Head, particularly in baseline air (84%). Peroxy radical production at night was also dominated by NO₃ reactions in baseline conditions (mean 89%), although the total production rate was very low compared with non-baseline conditions (mean value 6.0×10^3 molecules cm⁻³ s⁻¹). In non-baseline air, the NO₃ and O₃ oxidation mechanisms contributed approximately equally to

peroxy radical production for most of the night, and peroxy radical production rates were comparable to those observed in EASE 97 (mean total 6.7×10^4 molecules $\text{cm}^{-3} \text{s}^{-1}$). The estimated rate of peroxy radical production in baseline air was 5 times lower than non-baseline air for the NO_3 mechanism, and 50 times lower for the O_3 mechanism.

7.2 Suggestions for Further Research

7.2.1 Laboratory work

Further experiments using different PERCA inlet surfaces are required in order to determine for certain that the CLN-humidity effect is caused primarily by wall losses of HO_2 . To this end, a PERCA inlet has recently been constructed, based on the current glass design size specifications, but constructed from Teflon; the problem remains to find a way of controlling its temperature to enable a full set of experiments to be undertaken. Another possible approach would be to change the PERCA inlet design more radically, in particular to increase markedly the diameter of the inlet, thus reducing its surface area/volume ratio and consequently the importance of wall losses.

7.2.2 Humidity correction

In the event that the PERCA inlet design remains the same, the best method of correcting the ambient PERCA measurements in humid air must be investigated. In theory, the raw PERCA data could be corrected with the time resolution of the available meteorological data (dew point or relative humidity and temperature), *i.e.*, every minute. However, the PERCA CLN is usually measured only every few days in the field (see Chapter 5), with the CLN values interpolated for days between calibrations, so that daily CLN correction using averaged temperature and humidity data might be more appropriate.

7.2.3 Field campaigns

A further field campaign at Mace Head, to include PERCA and FAGE measurements, is already planned for summer 2002. Another spring campaign would also be useful, to supplement the results from ATAPEX (in 1995) and EASE 97, and to gain a broader picture of the interannual variability in ozone photochemistry under a range of pollution regimes by season. In addition, another field deployment of the scale of SOAPEX 2 at Cape Grim would be highly desirable, in order to sample the ultra-clean conditions that are frequently encountered at the site, but which were sadly lacking in January-February 1999.

Appendix – Calculation of specific humidity from relative humidity and temperature

Specific humidity, denoted q , is the ratio of the mass of water vapour to the total mass of a moist air parcel. Since the moist air and water vapour occupy the same total volume, q is also the ratio of the water vapour density to moist air density. Assuming that the ideal gas equation is applicable, we find that:

$$q = 0.623e/P \quad (A1)$$

where P is the total atmospheric pressure and e is the water vapour pressure, both in millibars (mb), and the relative molecular mass of air is assumed to be 28.9 (78% N_2 , 22% O_2). Similarly, the specific humidity of saturated air, q_s , is given by:

$$q_s = 0.623e_s/P \quad (A2)$$

where e_s is the saturation water vapour pressure. Since the pressure and density of the saturated vapour depend only on temperature, any given water vapour pressure at a given temperature represents a set fraction of the vapour pressure needed to achieve saturation at that temperature. This is termed the relative humidity, RH (%), of the air parcel:

$$RH = 100e/e_s \quad (A3)$$

Combining Equations (A1) and (A3), we obtain:

$$q = (0.623e_s/P).(RH/100) \quad (A4)$$

The saturation vapour pressure, e_s , at temperature T is calculated using the Clausius-Clapeyron equation [*e.g.*, *Atkins*, 1998]:

$$de_s/dT = (Le_s)/(R_v T^2) \quad (A5)$$

where L is the specific latent heat of vaporisation of water (2.5 MJ kg^{-1}) and R_v is the specific gas constant for water vapour ($462 \text{ J K}^{-1} \text{ kg}^{-1}$). Since the saturation vapour pressure of water at 273 K is 6.11 mb , on integration of Equation (A5) between 273 K and some higher temperature T , we obtain:

$$e_s(T) = 6.11 \cdot \exp\{(L/R_v)(1/273 - 1/T)\} \quad (\text{A6})$$

Finally, combining Equations (A4) and (A6), the following expression is obtained for calculation of specific humidity from relative humidity at temperature T :

$$q = [0.038 \cdot \exp\{L/R_v (1/273 - 1/T)\}] \cdot (RH/100) \quad (\text{A7})$$

The resulting q value is in kg kg^{-1} ; the specific humidities quoted in this thesis were converted to g kg^{-1} by multiplying by a factor of 1000.

Publications

Monks, P.S., **G. Salisbury**, G. Holland, S.A. Penkett and G.P. Ayers, A seasonal comparison of ozone photochemistry in the remote marine boundary layer, *Atmos. Environ.*, **34**, 2547-2561, 2000.

Savage, N., R.M. Harrison, P.S. Monks and **G. Salisbury**, Steady-state modelling of hydroxyl radical concentrations during the EASE 97 campaign, May 1997, *Atmos. Environ.*, **35**, 515-524, 2001.

Salisbury, G., A.R. Rickard, P.S. Monks, B.J. Allan, S. Bauguitte, S.A. Penkett, N. Carslaw, A.C. Lewis, D.J. Creasey, D.E. Heard, P.J. Jacobs and J.D. Lee, Production of peroxy radicals at night *via* reactions of ozone and the nitrate radical in the marine boundary layer, *J. Geophys. Res.*, in press, 2001.

Salisbury, G., P.S. Monks, S. Bauguitte, B.J. Bandy and S.A. Penkett, A seasonal comparison of the ozone photochemistry in clean and semi-polluted air masses at Mace Head, Ireland, submitted to *J. Atmos. Chem.*, November 2000.

Rickard, A.R., **G. Salisbury**, P.S. Monks, S. Bauguitte, B.J. Bandy, S.A. Penkett and A.C. Lewis, Comparison of measured ozone production efficiencies in the marine boundary layer at two European coastal sites under different pollution regimes, submitted to *J. Atmos. Chem.*, January 2001.

Carslaw, N., D.J. Creasey, D.E. Heard, P.J. Jacobs, J.D. Lee, A.C. Lewis, J.B. McQuaid, M.J. Pilling, S. Bauguitte, S.A. Penkett, P.S. Monks and **G. Salisbury**, Modelling the concentrations of OH, HO₂ and RO₂ during the EASE 97 campaign: 1. Comparison with measurements, submitted to *J. Geophys. Res.*, April 2001.

Postgraduate Record

Departmental Seminars

'High-resolution spectroscopy and bond breaking', Prof. T. Miller (University of Ohio), May 26 1998 (Bourke Lecture)

'The role of chemistry in the development of boron neutron-capture therapy', Prof. M.F. Hawthorne (UCLA), October 5 1998 (Royal Society of Chemistry Centenary Lecture)

'Cavity ring-down spectroscopy - applications to molecular dynamics and atmospheric chemistry', Dr A. Orr-Ewing (University of Bristol), October 7 1998 (RSC Lecture)

'The shape of things to come' – heterogeneous catalysis, combinatorial chemistry, single-electron devices, Prof. B. Johnson (University of Cambridge), October 26 1998 (RSC Lecture)

'Molecules with moving parts: the race for molecular machinery', Prof. D. Leigh (University of Warwick), April 3 2000 (RSC Lecture)

'Introduction to SciFinder Scholar', Dr B. Dunne (CAS), September 7 2000

'Chaos, Lyapunov exponents and transport coefficients', Prof. D.J. Evans (Australian National University), October 11 2000 (RSC Boys-Rahman Lecture)

'Ligand field theory in the new millennium: is there life after density functional theory', Dr R. Deeth (University of Warwick), November 27 2000

Physical Chemistry Seminars

1997-98 3rd-year postgraduate talks, May 1998

1997-98 2nd-year postgraduate talks, October 14 1998

'Recent advances in the study of chemical surfaces and interfaces by specular neutron reflection', Dr J. Penfold (ISIS-CLRC), November 11 1998

'Studies of atmospheric photochemistry and composition in clean air', Prof. S.A. Penkett (UEA), November 18 1998

1998-99 2nd-year postgraduate talks, April 28 1999

1998-99 3rd-year postgraduate talks, May-June 1999

'Investigation of transient molecules and radicals in the gas phase', Prof. F. Turecek (University of Washington), May 26 1999

‘Water clusters: little drops make a big splash!’ Prof. D. Clary (University College, London), October 20 1999

‘Timescales in atmospheric chemistry’, Prof. M.J. Pilling (University of Leeds), November 17 1999 (RSC Lecture)

‘New ways of looking at molecular structure’, Prof. G. Richards (University of Oxford), December 15 1999 (RSC Lecture)

1999-00 1st-year postgraduate talks, January 12 2000

‘Molecular functionalisation of electrode surfaces’, Dr R. Nichols (University of Liverpool), February 02 2000

‘NMR of liquid crystalline samples: a route to determining structures of molecules in a liquid state’, Prof. J. Emsley (University of Southampton), February 16 2000

1999-2000 2nd-year postgraduate talks, May 3 2000

1999-2000 3rd-year postgraduate talks, May 2000

‘Using templates to change the shapes of macromolecules’, Prof. T.C. Cosgrove, (University of Bristol), November 15 2000

‘Exploiting protein structure in the post-genome era’, Dr M.J.E. Sternberg (Imperial Cancer Research Fund), November 22 2000

‘Transition-metal chemistry in the gas phase’, Prof. A. Stace (University of Sussex), January 17 2001

‘Solids with mobile ions: can chemists be interesting and useful?’ Prof. P. Bruce (University of St Andrews), January 31 2001

‘Is the hydrogen bond unique? The case for a halogen bond’, Prof. A. Legon (University of Exeter), February 14 2001

‘The atmosphere: from shooting stars to ocean waves’, Prof. J.M.C. Plane (University of East Anglia), February 28 2001

Meetings/Conferences

FRACAS (FREE RADICALS in ACSOE) meeting, May 27 1998, with representatives from Leeds, Cambridge, UEA and Leicester (Leicester)

Meeting with Richard Crowther (UEA) and Dr P.S. Monks about analysis of data/modelling from EASE 96, August 26 1998 (Leicester)

SOAPEX pre-campaign meeting, October 23 1998, with representatives from Leeds, UEA and Leicester (Leicester)

SOAPEX mid-campaign meeting, February 11 1999, with representatives from Leeds, UEA, Leicester, Cape Grim staff and CSIRO (Smithton, Tasmania)

SOAPEX post-campaign meeting, February 24-25 1999, with representatives from Leeds, UEA, Leicester, Cape Grim staff and CSIRO (Melbourne, Victoria)

Annual meeting of the Royal Society of Meteorology Specialist Group in Atmospheric Chemistry, April 5 1999, with representatives from academic institutions throughout the U.K. (Cambridge)

ACSOE (Atmospheric Chemistry Studies in the Oceanic Environment) Scientific Symposium and EUROTRAC-2 Meeting, July 12-16 1999, with delegates from many U.K. universities and institutions abroad (UEA, Norwich)

Meeting with Philip Jacobs and Dr Nicola Carslaw (University of Leeds) and Dr P.S. Monks on analysis of the Mace Head data, October 25 1999 (Leicester)

FREETEX (Free Troposphere Experiment) 2001 meeting, with representatives from the Universities of East Anglia, Leicester and Bern, November 24-26 1999 (Bern, Switzerland)

SOAPEX final meeting, January 6-7 2000, with representatives from Leeds, UEA, Leicester and Cambridge (Leeds)

Annual meeting of the Royal Society of Meteorology Specialist Group in Atmospheric Chemistry, April 17 2000, with representatives from academic institutions throughout the U.K. (Leicester)

Remote Sensing Society Annual Conference, September 13 2000, with representatives from academic institutions throughout the U.K. (Leicester)

4th Upper Troposphere – Lower Stratosphere (UTLS) meeting, December 18-20 2000, with delegates from many U.K. universities and institutions abroad (Leicester)

Annual meeting of the Royal Society of Meteorology Specialist Group in Atmospheric Chemistry, April 10 2001, with representatives from academic institutions throughout the U.K. (Nottingham Trent)

Presentations (all given at Leicester unless noted)

Group talk on peroxy radical measurements in the troposphere, June 30 1998

1st-year postgraduate talk, October 14 1998

PERCA progress report for SOAPEX planning meeting, October 23 1998

Progress report for SOAPEX mid-campaign meeting, February 11 1999 (Cape Grim)

Campaign summary talk for SOAPEX post-campaign meeting, February 24 1999 (CSIRO, Melbourne)

Group talk on night-time atmospheric chemistry, December 6 1999

Presentation of first data analysis for SOAPEX final meeting, January 7 2000 (University of Leeds)

2nd-year postgraduate talk, January 12 2000

3rd-year postgraduate talk, October 18 2000

'Peroxy radical measurements in the marine boundary layer', January 10 2001 (Max Planck Institute for Chemistry, Mainz)

Posters

Salisbury, G., J.J. Clark and P.S. Monks, *Analysis of pollution tracers and peroxy radicals during EASE 96 and EASE 97*, presented during the ACSOE Scientific Symposium, July 12-16 1999 (UEA, Norwich)

Rickard, A.R., G. Salisbury and P.S. Monks, *Ozone production efficiencies at two European coastal sites*, presented by Dr A.R. Rickard at the EUROTRAC TOR-2 Workshop, September 23-26 2000 (Dubrovnik, Croatia)

Taught Courses

Earth Observation Science MSc Module 701 (Introduction): Introduction to Atmospheric Chemistry (Dr P.S. Monks); Space Techniques (Prof. D. Llewellyn-Jones); Introduction to Oceans and Ice/Meteorology and Modelling (Dr S. Lawrence); Earth as a Global System (Dr J. Wellands)

Earth Observation Science MSc Module 705: Introduction to Programming in C (Mr W. Rathman)

Earth Observation Science MSc Module 706: Atmospheric Chemistry (Dr P.S. Monks)

A Course for Demonstrators – June 14 2000 (Dr N. Beasley, Staff Development)

Examinations

Earth Observation Science – The Atmosphere, Chemistry and Dynamics (2 papers), April 14-15 1999

1st-year *viva voce* examination – May 30 1999 (Dr A.M. Ellis)

Postgraduate Committee Meetings

1st year – August 28 1998

2nd year – November 3 1999

3rd year – July 5 2000

Collaborative Experiments

PERCA characterisation experiments with Dr Prodromos Zanis, University of Bern, Switzerland, July-August 1998 (Leicester)

Comparison of peroxy radical sources with Leeds FAGE group (Dr James Lee), September 21–22 1998 (Leicester)

Absolute calibration of PERCA field photolysis unit with Dr Tim Green, University of East Anglia, June 3-4 1999 (UEA, Norwich)

Cross-calibration of PERCA with UEA Aircraft PERCA instrument with Dr Tim Green, University of East Anglia, June 28-30 1999 (Leicester)

Postgraduate Training Programme

(Module CH501: Research Techniques)

Introduction/Safety – Prof. P.Cullis, Dr J. Malpass, Mrs D. Sutherland, September 28 1998

Introduction to Key Techniques and Equipment – Mr M. Lee, Dr G. Eaton, Dr J. Fawcett, Dr G. Griffith, September 29 1998

Introduction to COSHH assessments – Mrs N. Bhanji, October 2 1998

Fire Safety Lecture and Practical – Fire Safety Officer, November 4 1998

N.M.R. Techniques 1: 1D N.M.R. – Dr G. Griffith, December 2 1998

N.M.R. Techniques 3: The Nuclear Overhäuser Effect - Dr G. Griffith, March 29 1999

Endnote – Dr D.L. Davies, June 2 1999

Advanced Scientific Writing – Dr J.R. Malpass, June 9 1999

N.M.R. Techniques 4: Data Presentation – Dr G. Griffith, June 16 1999

ChemDraw, Molecular Modelling and Powerpoint – Prof. P.M. Cullis, March 08 2000

BIDS/MIMAS, Crossfire and Beilstein – Dr E. Raven and Dr G.A. Solan, April 12 2000

References

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Carslaw, N., N. Bell, A.C. Lewis, J.B. McQuaid and M.J. Pilling, A detailed case study of isoprene chemistry during the EASE 96 Mace Head campaign, *Atmos. Environ.*, **34**, 2827-2836, 2000.

Carslaw, N., D.J. Creasey, D.E. Heard, P.J. Jacobs, J.D. Lee, A.C. Lewis, J.B. McQuaid, M.J. Pilling, S. Bauguitte, S.A. Penkett, P.S. Monks and G. Salisbury, Modelling the concentrations of OH, HO₂ and RO₂ during the EASE 97 campaign: 1. Comparison with measurements, submitted to *J. Geophys. Res.*, 2001a.

Carslaw, N., P.J. Jacobs, M.J. Pilling and D.E. Heard, Modelling the concentrations of OH, HO₂ and RO₂ during the EASE 97 campaign: 2. Insight into radical chemistry, submitted to *J. Geophys. Res.*, 2001b.

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