Modelling of tropospheric ozone and radical chemistry
- Modellierung der troposphärischen Ozon- und Radikalchemie-

Vom Fachbereich für Physik und Elektrotechnik der Universität Bremen

Zur Erlangung des akademischen Grades eines Doktor der Naturwissenschaften (Dr. rer. nat.) genehmigte Dissertation

von
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Eingereicht am: 10.03.2003
Tag des Promotionskolloquiums 16.04.2003
Abstract

This work describes in detail the photochemistry of O₃ and radicals in both remote “clean air” and “heavily polluted” regions. The results of two field studies are presented: the Indian Ocean Experiment (INDOEX) and the Peroxy Radical Initiative for Measurements in the Environment (PRIME).

The INDOEX campaign, an international research initiative, studied the chemistry of remote areas of the Indian Ocean and the influence of the outflow from the Indian subcontinent on these regions. Within the INDOEX campaign the first measurements of peroxy radicals were successfully performed above the Indian Ocean. These, together with other relevant trace gases (NMHC, O₃, CO, HCHO, NO, O₃ soundings, and satellite data of O₃, HCHO, and NO₂) and parameters (j(NO₂), j(O(¹D)), and meteorological data) have been compared with the results of a 0-dimensional chemistry model. The comparison between measurements and simulations revealed large discrepancies, which indicated the presence of significant levels of Cl (10⁴-10⁵ molecule cm⁻³).

In addition, a radiative transfer model has been modified and used to calculate the influence of highly absorbing aerosols on the energy budget of the Earth. The results of the RTM calculations of the warming rates caused by the aerosols’ absorption of solar radiation showed temperature increases up to 1 K. This temperature increase particularly above the MBL stabilised the atmosphere significantly. Therefore, the presence of aerosols in the layer above the MBL leads to enhanced stability during the day and less stability during the night.

Satellite and sonde data were used for the investigation macro and mesoscale processes and for the identification of all relevant processes responsible for the amount of O₃ present above the Indian Ocean. The combination of vertical profiles, satellite pictures of tropospheric columns of O₃, NO₂, HCHO, and meteorological data, indicated that the amount of O₃ resultant from the STE is the major source for tropospheric O₃ in the SH Indian Ocean.

The PRIME campaign took place during July and August 1999 near London, UK. Ambient measurements of trace gases (HO₂, RO₂⁺, NO₂, NO, PAN, CO, CH₃OOH, H₂O₂, OH) were carried out.

During daylight the maximum RO₂⁺ mixing ratios varied between 15 and 70 pptv during “polluted episodes”. At night non negligible amounts of RO₂⁺ were observed, varying between 5 to 20 pptv.

The comparison between simulated and measured daytime trace gas concentrations showed good agreement for RO₂⁺, H₂O₂, OH and large discrepancies for HO₂. The measured RO₂⁺ to HO₂ ratio varied between 5 to 10, which is in total disagreement with the model results where this ratio varied between 1.1 and 2.3 even when the model was run with unrealistically high amounts of volatile organic compounds. The measured H₂O₂ mixing ratios are also in disagreement with the observed HO₂ amounts assuming that H₂O₂ is exclusively produced via the HO₂ self reaction.

The actual measurements of RO₂⁺, HO₂, and NO taken during the early morning hours showed that these three species coexisted in high amounts. This cannot be explained by the known chemistry.
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Chapter 1: Introduction and overview

1 Introduction and overview

1.1 Introduction

Over the last decades, the growing realisation that human activities influence the chemical composition of the atmosphere has led to more scientific attention towards the physical and chemical processes within the Earth’s atmosphere. The ozone hole discovered by Farman et al. [1985], the destruction of forests by acid rain [Brimblecombe, 1977, Cowling, 1982] or the observation of summer smog situations in Los Angeles by Haagen-Smit [1952] are indicative of the extent to which mankind has influenced and been detrimental to life on this planet. Knowledge of the dominant atmospheric processes is essential prerequisite for predicting the anthropogenic influence on the climate system and therefore on the future of our planet Earth.

The “main constituents” of air have been known for a long time, Table 1 gives an overview of the mixing ratios of individual gases. The main components are relatively inert gases, that contribute little to chemical reactions and therefore to the behaviour of the atmosphere.

<table>
<thead>
<tr>
<th>Gases</th>
<th>Mixing ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>78.084 Vol %</td>
</tr>
<tr>
<td>Oxygen</td>
<td>20.946 Vol %</td>
</tr>
<tr>
<td>Argon</td>
<td>0.934 Vol %</td>
</tr>
<tr>
<td>Carbon dioxyde</td>
<td>360 ppmv¹</td>
</tr>
<tr>
<td>Neon</td>
<td>18.18 ppmv</td>
</tr>
<tr>
<td>Helium</td>
<td>5.24 ppmv</td>
</tr>
<tr>
<td>Methane</td>
<td>1.6 – 1.8 ppmv</td>
</tr>
<tr>
<td>Krypton</td>
<td>1.14 ppmv</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.5 ppmv</td>
</tr>
<tr>
<td>Other trace gases</td>
<td>~ 0.3 ppmv</td>
</tr>
</tbody>
</table>

Table 1: Main compounds of dry air [Brimblecombe, 1986].

¹ ppmv = parts per million (v/v)
Because of this the focus is on the so called “trace gases”. Table 2 shows the observed mixing ratios of several trace gases divided into the clean and polluted troposphere and the stratosphere.

<table>
<thead>
<tr>
<th>Gas Name</th>
<th>Chemical Formula</th>
<th>Clean Troposphere</th>
<th>Polluted Troposphere</th>
<th>Stratosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water vapour</td>
<td>H₂O</td>
<td>3000-4.0(+7)</td>
<td>5.0(+6)-4.0(+7)</td>
<td>3000-6000</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>365,000</td>
<td>365,000</td>
<td>365,000</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>40-200</td>
<td>2000-10,000</td>
<td>10-60</td>
</tr>
<tr>
<td>Ozone</td>
<td>O₃</td>
<td>10-100</td>
<td>10-350</td>
<td>1000-12,000</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>SO₂</td>
<td>0.02-1</td>
<td>1-30</td>
<td>0.01-1</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>NO</td>
<td>0.005-0.1</td>
<td>0.05-300</td>
<td>0.005-10</td>
</tr>
<tr>
<td>Nitrogen oxide</td>
<td>NO₂</td>
<td>0.01-0.3</td>
<td>0.2-200</td>
<td>0.005-10</td>
</tr>
<tr>
<td>CFC-12</td>
<td>CF₂Cl₂</td>
<td>0.55</td>
<td>0.55</td>
<td>0.22</td>
</tr>
<tr>
<td>Organic</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>1800</td>
<td>1800-2500</td>
<td>150-1700</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>0-2.5</td>
<td>1-50</td>
<td>---</td>
</tr>
<tr>
<td>Ethene</td>
<td>C₂H₄</td>
<td>0-1</td>
<td>1-30</td>
<td>---</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>HCHO</td>
<td>0.1-1</td>
<td>1-200</td>
<td>---</td>
</tr>
<tr>
<td>Toluene</td>
<td>C₆C₅CH₃</td>
<td>---</td>
<td>1-30</td>
<td>---</td>
</tr>
<tr>
<td>Xylene</td>
<td>C₆H₄(CH₃)₂</td>
<td>---</td>
<td>1-30</td>
<td>---</td>
</tr>
<tr>
<td>Methyl chloride</td>
<td>CH₃Cl</td>
<td>0.61</td>
<td>1-30</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table 2: Variation in the amount of several trace gases in different parts of the atmosphere [Jacobson, 1998a].

The conversion of trace gases in the atmosphere is dominantly caused by radicals via catalytic cycles. The resultant products are stable species such as carbon dioxide (CO₂) or water soluble compounds like sulphuric acid (H₂SO₄) or nitric acid (HNO₃). The steady increase of anthropogenic emissions of relatively long lived species like methane (CH₄) with an atmospheric lifetime (τ) of ~10.5 years, carbon monoxide (CO) (τ ~ 3 month), and nitrogen oxides (NO, NO₂) (τ ~ few days) [IPCC, 1992] causes
the majority of known effects like global warming (CO$_2$) or acid rain (H$_2$SO$_4$, HNO$_3$). These effects then in turn exert a lasting influence on the biosphere and the climate. The understanding of the reaction pathways between the mainly anthropogenic emitted gases (CH$_4$, CO, NO, NO$_2$) and the stable species like CO$_2$, H$_2$SO$_4$, and HNO$_3$, is an essential part of the process of developing strategies to reduce the emission of gases harmful for human health and/or climate.

In the troposphere the decomposition of nearly all trace gases is caused by the reaction with OH, O$_3$, and NO$_3$. Knowledge of processes like CO oxidation (through the reaction of CO with OH radicals [Weinstock, 1969]) or the production of OH radicals (via the photolysis of O$_3$ and the subsequent reaction with water (H$_2$O) [Levy, 1971]), the importance of radicals has become central to the understanding of tropospheric chemistry. Furthermore, peroxy radicals are the key intermediates of all oxidation processes taking place in the Earth’s atmosphere, and are therefore the crucial species on which to base any verification of the current knowledge and understanding of processes – for example by comparing model results with observations.

The different levels of anthropogenic pollution found in the troposphere makes it easier to understand the dominant chemical processes. This is why in heavily polluted areas (for example, large conurbations or industrial centres) reactions involving nitrogen oxides are emphasized because of the relatively high amounts of NO$_x$ (=NO+NO$_2$) mixing ratios (~20 ppbv) present.

Conversely, in less polluted regions (for example, areas of low population and industrial density) trace gas mixing ratios (NO$_x$ ~ 1 ppbv) are mainly influenced by emissions of biochemical degradation products of plants and animals. However it is not possible to neglect this type of reactions in favour of those dominating in polluted areas because reaction rates are often comparable.

The chemistry of remote “clean air” regions (for example above the oceans) is relatively simple. In these areas amounts of NO$_x$ are lowest (NO$_x$ ~ 0-40 pptv$^3$). In these

\footnotesize
\begin{itemize}
  \item 2 ppbv = parts per $10^9$ (v/v)
  \item 3 pptv = parts per $10^{12}$ (v/v)
\end{itemize}
“clean air” areas, reactions between $O_3$, OH, HO$_2$, and the degradation products of methane can become dominant over the NO$_x$ reactions concerning $O_3$ production and loss mechanisms. Therefore remote “clean air” regions are of special interest for the total tropospheric $O_3$ budget.

The absence of anthropogenic sources leads to the fact that the complex chemistry of non methane hydrocarbons (NMHC) and the dynamical processes play only a minor important role. The measurements in remote “clean air” regions provide the opportunity to observe the undisturbed evolution of trace gas concentrations over the time period of several days. This then enables comparisons to be made between measurements and model calculations, the results of which help to identify hitherto unknown processes relevant to the chemistry of the Earth’s atmosphere.
1.2 Overview

The aim of this work is to describe in detail the photochemistry of O$_3$ and radicals in both remote “clean air” and “heavily polluted” regions. The results of two field studies are presented which form the basis for this thesis. These studies were the Indian Ocean Experiment (INDOEX)$^4$ and the Peroxy Radical Initiative for Measurements in the Environment (PRIME)$^5$.

Within the INDOEX campaign the first measurements of peroxy radicals \( RO_2^* = HO_2 + \sum_i R_iO_2 \) were successfully performed above the Indian Ocean. These, together with other relevant trace gases and parameters have been compared with the results of a 0-dimensional chemistry model developed within this work (for details see Appendix 0). The comparison between measurements and simulations revealed large discrepancies, which lead to the identification of new processes of relevance to the chemistry of the atmosphere. In addition, a radiative transfer model has been modified and used to calculate the influence of highly absorbing aerosols on the energy budget of the Earth. Satellite and sonde data have been used for the investigation of large scale phenomena and for the identification of all relevant processes responsible for the amount of O$_3$ present above the Indian Ocean.

The measurements of PRIME complement the peroxy radical dataset obtained during the INDOEX campaign by providing radical datasets for polluted urban air mass, i.e. the outflow of London, UK. The PRIME study analysed the measured variability of radical, peroxy radical, and peroxide mixing ratios by the comparison with model results.

$^4$The INDOEX campaign, an international research initiative, studied the chemistry of remote areas of the Indian Ocean and the influence of the outflow from the Indian subcontinent on these regions [see Crutzen and Ramanathan, 2001, Ramanathan et al., 2001, Lelieveld et al., 2001, Ball et al., 2003, http://www-indoex.ucsd.edu]. This campaign took place during February, March, and April 1999.

$^5$The PRIME campaign took place during July and August 1999 at the Silwood Park Atmospheric Research Station, near London (51°24’53”N, 0°38’48”W). The site offered the opportunity to measure on many days the plume from the city centre of London.
The large discrepancies between measured and simulated hydrogen peroxy radical concentrations and the coexistence of high amounts of nitrogen oxides and peroxy radicals are the two main features observed. Different processes are suggested to explain the disagreement between measured and expected (i.e. by the conventional tropospheric chemistry) concentrations.

The outline of this work is as follows: Chapter 2 presents in some detail the theoretical background of this work. The theoretical background highlights the limitations in the current scientific knowledge and the questions that need to be solved.

Chapter 3 gives an overview of the different measurement techniques and model specifications used within the PRIME and INDOEX campaign.

The INDOEX campaign is described in Chapter 4. In the first section the analysis of the peroxy radical and formaldehyde (HCHO) measurements is shown, based on Burkert et al. [2003a]. Diurnal behaviour of O₃ and the responsible meso scale processes follow and finally the chapter ends with a discussion on the possible sources for O₃ and the influence of highly absorbing aerosols on the energy budget of the Earth [Burkert et al., 2003b].

Chapter 5 focuses on the interpretation of the measurements of RO₂⁺, HO₂, OH, and H₂O₂ from the PRIME campaign, in particular on the difference between simulations and measurements [Burkert et al., 2003c].

Chapter 6 summarises this work and describes the most striking features found. It also includes a discussion on the limitations of the current understanding of atmospheric chemistry and dynamics concluding with an overview of open questions and recommendations resultant from this work.
2 Theoretical background

The chapter that follows is an overview and discussion on the theoretical background which underpins this research. The material is divided into two main sub-sections - “Physics of the atmosphere” (2.1) and “Chemistry of the troposphere” (2.2).

2.1 Physics of the atmosphere

This section is comprised of two sub-sections - “Radiation and energy processes” (2.1.1) and “Dynamics of the atmosphere” (2.1.2). The intention in this discussion is not to cover everything about these two very large fields of physics, but rather to discuss processes which are later used as the basis for the interpretation and modelling of the natural phenomena encountered during the course of the research.

2.1.1 Radiation and energy processes

Radiation and energy processes are fundamental to even a simplistic understanding of radiative transfer models. Furthermore, radiation and energy budgets are necessary in order to comprehend the dynamical mechanisms described in chapter 2.1.2. One of the more important theoretical concepts is the frequently underestimated role that the scattering and absorption of aerosols play in this budgets.

2.1.1.1 Basics of the radiative transfer

Absorption and scattering are the two most crucial processes influencing the radiation in the atmosphere. Thermal emission plays only a minor role, at least in the UV and visible wavelength region. Thermal emissions are therefore excluded from the following discussions.

**Absorption** is the interaction between a photon and solid or fluid matter or gases, in a process that results in the photon being picked up by a molecule or atom. The molecule changes its structure and emits excess energy in various ways.
For the molecule AB in the excited state AB\(^*\) the ways of emitting excess energy are:

- Fluorescence: \(AB^* \rightarrow AB + h\nu\)
- Photoionisation: \(AB^* \rightarrow AB^+ + e^-\)
- Reaction: \(AB^* + C \rightarrow AC + B\)
- Quenching: \(AB^* + M \rightarrow AB + M\)
- Photodissociation: \(AB^* \rightarrow A + B\).

The probability of the absorption of a photon with a certain wavelength by a molecule is dependent on the molecule’s structure. The describing parameter for the molecule’s structure is the absorption cross section \(\alpha(\lambda)\), measured in units of \(\text{cm}^2\text{molec}^{-1}\).

A molecule absorbs only photons with certain discrete energies – a phenomena caused by the different energy states of the molecule. In the UV / visible light region of the spectrum continuous spectra are often observed. These spectra are caused by excitation of a molecule by a photon in an unbound state. This excitation leads to dissociation of the molecule and in consequence to non discrete energy differences.

The number density (concentration) \(N\) in [molec cm\(^{-3}\)] of an atmospheric gas also has a significant influence on the attenuation of sunlight as it passes through the atmosphere. The product of the absorption cross section \(\alpha(\lambda)\) and number density \(N\) is named absorption coefficient \(a(\lambda)\) in units of [cm\(^{-1}\)].

Scattering is the interaction between light and solid or fluid matter, which occurs whenever a photon changes its direction. If a photon is elastically scattered, the energy (i.e. the wavelength) will be conserved. By contrast inelastic scattering occurs when change in the direction of the photon is accompanied by an energy transfer between the photon and the scattering molecule.

In the following discussions only elastic scattering is considered. This is because inelastic scattering plays only a minor role in the process under review here.

The two main quantities used to describe scattering are the effective scattering cross section \(\beta(\lambda)\) and the phase function \(p(\gamma)\). The scattering cross section has the same units as the absorption cross section and therefore described in units of [molec cm\(^2\)].
In analogy to the absorption, the scattering coefficient represents the attenuation of light through the product of the scattering cross section $\beta(\lambda)$ and the number density $N$ of the scattering centres. Each air molecule works as a scattering centre and the scattering coefficient is therefore proportional to the air pressure.

Phase function is a way of representing the directional dependence of the scattered radiation as a function of the scattering angle $\gamma$. It is usual to express phase function by normalising it to unity. Put in another way, phase function is the probability of a photon being scattered in a certain direction, and the scattering angle $\gamma$ is the angle between incoming and outgoing radiation.

Scattering is divided into two types (Rayleigh and Mie scattering) - defined by the relative proportion between the size of the scattering centre and the wavelength of the light. For both types the resultant scattering cross sections and phase functions are different.

When the scattering particles are small compared to the wavelength, the scattering is described by the Rayleigh scattering theory. The theory is based on the assumption that the light is scattered by spherical particles. In the simplest case of spherical particles the phase function for Rayleigh scattering has the form

$$p, (\gamma) = \frac{3}{4}(1 + \cos^2\gamma).$$

However, the two most important scattering particles $O_2$ and $N_2$ are linear molecules, therefore a correction factor has to be included. This factor is a function of the so called depolarisation factor $\delta$.

Taking the formula of Rayleigh and Cabannes for the Rayleigh scattering cross section (note that this formula also includes the refractive index that depends on pressure and temperature [Penndorf, 1957]), the scattering cross section for Rayleigh scattering is approximately proportional to $\lambda^{-4}$. Hence the blue colour of a clear sky results from the stronger scattering of shorter wavelengths.

Rayleigh scattering is relatively isotropic (isotropic: $p(\gamma)=$const.). As a result of this, nearly equal amounts of light are scattered forward and backwards, and about half of the forward or backward scattered light is vertical to the incoming radiation scattered.

The second type of scattering is named Mie scattering. The Mie theory is used when the size of the scattering particles is in the same range of the wavelength of the light. Examples of Mie scattering particles in the atmosphere are the aerosols or cloud...
droplets. The dependence of the scattering coefficient on the wavelength is between $\lambda^{-1}$ and $\lambda^{-1.5}$, depending on the particle size. Compared to the Rayleigh scattering the wavelength dependence is much smaller. The most visible consequence of this type of scattering is the white colour of clouds. In addition the phase function of Mie scattering by contrast to Rayleigh scattering has a distinct forward scattering behaviour.

The extinction coefficient $\sigma_e(\lambda)$ results from the effective coefficient from the absorption ($a(\lambda)$) and scattering ($b(\lambda)$).

$$\sigma_e(\lambda) = a(\lambda) + b(\lambda)$$  \hspace{1cm} (2)

The integral of $\sigma_e(\lambda)$ over the optical path (usually the height $z$) is called optical depth $\tau(\lambda, z)$

$$\tau(\lambda, z) = \int_z^\infty \sigma_e(\lambda, z') dz'$$  \hspace{1cm} (3)

and in several formulations of the radiative transport the optical depth is used as an independent variable instead of the geometrical height [e.g. Sobolev, 1975, Meier et al., 1982, Stamnes et al., 1988].

Resultant from the optical depth there comes the optical thickness $\tau(\lambda)$, defined as the specific integral of the optical depth between $z_1$ and $z_2$ for a given medium.

The ratio between scattering and extinction coefficient is named single scattering albedo

$$\sigma_o(\lambda) = \frac{b(\lambda)}{\sigma_e(\lambda)}.$$  \hspace{1cm} (4)

This parameter represents the probability of scattering occurring when a photon interacts with a molecule in the atmosphere. Media with $\sigma_o(\lambda) = 1$ (i.e. no scattering), are conservative.

### 2.1.1.2 Radiation/Energy budget

The radiation from the Sun is the ultimate source of energy which drives the Earth’s climate. About 90% of the sun’s radiant energy lies within the 0.4 to 4 µm wavelengths - maximum intensity being in the green part of the visible spectrum (at 0.48 µm – Figure 1).
Assuming the Earth had no atmosphere and a spherical surface, each square metre would receive on average 342 Watts of solar radiation throughout the year. The atmosphere approximately halves this number, because about 30% of the incoming solar energy is reflected back into space by clouds, the atmosphere, and by the Earth’s surface. Approximately 20% of the sun’s incoming energy is absorbed by the atmosphere but most of it (~168 Wm$^{-2}$) penetrates the atmosphere and warms the Earth’s surface: both the land and the oceans.

Energy returns to the atmosphere from the Earth’s surface by means of infrared radiation, sensible heat, and as water vapour - which releases its heat to the atmosphere as it rises and condenses.

The mean global temperature near the ground which results from these processes is about 14°C. This decreases rapidly with increasing altitude, reaching a mean temperature of ~58°C at the top of the troposphere.
Energy balance is achieved when the climate system itself radiates on average 235 Wm$^{-2}$ back to space. Figure 2 details these energy balancing processes - the left hand side shows what happens to the incoming solar radiation, with the right hand side showing how the atmosphere emits the outgoing infrared radiation.

![Figure 2: The greenhouse effect](image)

Figure 2: The greenhouse effect [colour image adapted from Kiehl and Trenberth, 1997]. The Earth’s radiation energy balance which controls the way the greenhouse effect works, can here be seen graphically. Note that nearly half the incoming solar radiation penetrates the clouds (and greenhouse gases) to reach the Earth’s surface. Greenhouse gases and clouds reradiate most of the absorbed energy back down toward the surface.

The Earth’s energy balance leads to an equilibrium climate state with a zero average net radiation at the top of the atmosphere (TOA). In practice, the top of the troposphere is taken as the top of the atmosphere. This is because the stratosphere responds faster (in the order of months) to changes in the radiative balance, in contrast to the Earth’s surface-troposphere system (with its large thermal inertia caused by the oceans).
Changes in either solar radiation or infrared radiation affect the net radiation, and therefore leads to an imbalance called “radiative forcing” – defined by IPCC as follows:

“The **radiative forcing** of the surface-troposphere system due to the perturbation in, or the introduction of, an agent (say, a change in greenhouse gas concentrations) is the change in net (down minus up) irradiance (solar plus long-wave; in Wm$^{-2}$) at the tropopause AFTER allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures, and state held fixed at the unperturbed values” [Intergovernmental Panel on Climate Change (IPCC), 1996].

### 2.1.1.3 Aerosol scattering and absorption

Atmospheric aerosol particles are of major importance for solar radiative transfer and thus affect the Earth’s climate. As a result, the so called direct aerosol effect refers to the reflection and absorption of solar radiation by these aerosols [e.g. Charlson and Heintzenberg, 1995]. Several studies have assessed the direct effect of aerosol particles in terms of their radiative forcing at the top of the atmosphere [for examples see IPCC, 1996].

The scattering and absorption of aerosols leads to differences in vertical temperature profiles. It is not possible to distinguish whether there is a positive or a negative feedback on the radiative forcing, because several parameters have to be considered (e.g. albedo, solar zenith angle, vertical profiles of the aerosols). In general scattering processes in the atmosphere control the portion of incoming radiation scattered back to space, and absorption processes control the transfer light to other energy forms, mainly heat. Consequently an increasing burden of scattering particles (e.g. sulfates) induces a net cooling effect [Charlson et al., 1991].

However if absorbing aerosols are also present in the atmosphere, cooling caused by an increase in scattering particles can be offset or even changed into a heating effect [Chylek and Coakley, 1974, Haywood and Shine, 1995].

One of the strongest absorbing components in the solar spectral range is black carbon (BC) [Bohren and Huffman, 1983]. BC is responsible for a significant fraction of light extinction in urban [Shah et al., 1984], rural [Trijonis, 1982], and remote continental areas [Malm et al., 1994]. As the average lifetime of BC particles is in the
range of a week (depending on the rate of mixing with other compounds and the rain rate), BC can also be found in remote polar and oceanic regions [Heintzenberg, 1982, Hansen and Novakov, 1988, Clarke, 1985].

Significant radiative forcing due to particle absorption can be expected in regions with high BC concentrations [Smith et al., 1989, Cadle and Dasch, 1988]. If the BC particles are embedded in nonabsorbing particles, they absorb solar radiation more efficiently than they could as separate BC particles [e.g. Fuller, 1999, Horvath, 1997, Heintzenberg and Wendisch, 1996].

In order to make quantitative estimates of the radiative forcing of the absorbing component of the particles, radiative transfer calculations have to be based on detailed measurements. Studies based on ground-based particle absorption measurements [e.g. Müller et al., 2000] can give estimates of the forcing for certain atmospheric conditions (e.g. well-mixed boundary layer).

The assessment of the radiative forcing of aerosol particles from the measured aerosol absorption properties is of special importance in climatic studies. As shown by Haywood and Shine [1997] and Haywood and Ramaswamy [1998], the direct radiative forcing is strongly dependent on BC vertical profiles. For example, BC in higher altitudes, above highly reflecting clouds, can induce a much higher forcing than BC located below clouds.

In addition to the direct radiative forcing at the TOA, the warming of different layers within the atmosphere is important. Absorption of aerosols is particularly important when investigating local dynamics, as it can lead to either a stabilising or destabilising effect dependent on the vertical structure and composition of the atmosphere. In polluted areas where absorbing aerosols are emitted within the lowest layers absorption by direct sunlight leads to increased heating in these layers (i.e. compared to the heating of air parcels above). As a consequence, absorbing aerosols can lead to an enhanced ascent of the lowest atmospheric layer, together with increased entrainment of free tropospheric air.

The opposite effect is observed in remote areas over the northern Indian Ocean. The marine boundary layer (MBL) contains mainly scattering aerosols (e.g. sea salt aerosols), which lead to a cooling effect. The layer above the MBL is characterised by highly absorbing aerosols. Thus the cooling in the MBL and the heating in the free troposphere lead to a stabilising effect, which results in entrainment being suppressed.
This effect was neglected in the past, but the calculations by Burkert et al. [2003b] indicate the importance of this effect when modelling at both local and global scales (especially in the Indian outflow region above the ocean).

A secondary effect of aerosols is called “indirect forcing”. This process involves the role of aerosol particles as cloud condensation nuclei [Ramanathan et al, 2001].

2.1.2 Dynamics of the atmosphere

This section focuses on an experimental view of the atmospheric dynamics. The following subsections consider the different parts of the troposphere separately: The boundary layer (chapter 2.1.2.1), the free troposphere (chapter 2.1.2.2), and the tropopause region (chapter 2.1.2.3).

![Diagram of vertical temperature profile of the Earth's atmosphere with labelled regions.]

Figure 3: The vertical temperature profile of the Earth’s atmosphere. The different regions are labelled.
The troposphere extends from the surface up to an altitude of 8 to 18 km (Figure 1). The transition zone between the troposphere and the stratosphere is named tropopause. The height of the tropopause is defined by the World Meteorological Organization (WMO) as the lowest level at which the rate of decrease of temperature with height (i.e. temperature lapse rate) decreases to 2 K km\(^{-1}\) or less and the lapse rate averaged between this level and any level within the next 2 km does not exceed 2 K km\(^{-1}\) [Holton et al., 1995]. The height of the troposphere is minimal at the pole and slopes upward towards the inter tropical convergence zone (ITCZ).

The temperature lapse rate within the troposphere is 9.8 K km\(^{-1}\) for dry air (dry adiabatic lapse rate (\(\Gamma_D\))). The reason for this progressive decline is the increasing distance from the Earth’s surface.

Vertical motion of air is caused by either (a) convection from solar heating of the Earth’s surface, (b) convergence or divergence of horizontal flows, (c) horizontal flow over topographic features at the Earth’s surface, and/or (d) buoyancy caused by the release of latent heat as water condenses [Seinfeld and Pandis, 1998].

As air moves vertically, its temperature changes in response to the local pressure. The “Ideal Gas Law” is a combination of Boyle’s law, Charles’ law, and Avogadro’s law, and describes the change of temperature and pressure as follows,

\[
p = \frac{nR^*T}{V} = \frac{nA}{V} \left( \frac{R^*}{A} \right) T = Nk_B T
\]

where \(R^*\) is the universal gas constant (8.314 x 10\(^4\) cm\(^3\) mbar mole\(^{-1}\) K\(^{-1}\)), \(A\) is the Avogadro’s number, \(A = 6.02252 \times 10^{23}\) molecules mole\(^{-1}\), \(N=nA/V\) is the number concentration of gas molecules (molecules of gas per cubic centimetre of air), and \(k_B = R^*/A\) is Boltzmann’s constant in units of 1.3807 x 10\(^{-19}\) cm\(^3\) mbar K\(^{-1}\).

The rate of change of temperature with height is dependent on the water content of the air parcel and therefore can vary between 5 (wet adiabatic lapse rate (\(\Gamma_W\))) and 10 K km\(^{-1}\) (dry adiabatic lapse rate). The vertical motion of air parcels accompanied with the strong dependence of the saturation vapour pressure on temperature can lead to an increase of the relative humidity (r.h.). This increase can cause the air to reach saturation (r.h. = 100%) or even supersaturation. The saturation of air leads to formation of clouds and therefore to additional energy win for the rising air parcel through the latent heat release as water condenses.
2.1.2.1 Atmospheric Boundary layer

The atmospheric boundary layer (ABL) is defined as the part of the troposphere that is directly influenced by the presence of the Earth’s surface and responds to surface forcing with a timescale of about an hour or less [Stull, 1988]. This forcing includes frictional drag, evaporation and transpiration, heat transfer, pollutant emission, and terrain induced flow modification. The ABL is capped by a statically stable layer of air or temperature inversion. The height of the inversion layer is variable in time and space, ranging from tens of metres in strongly statically stable situations, to several kilometres in convective conditions over deserts and oceans. Within the ABL strong turbulence is common.

The following discussion differentiates the characteristics of the ABL over land from those of the ABL over the ocean. The definition of the different meteorological parameters are according to the Glossary of Meteorology, 2nd Edition, American Meteorological Society [2000].

The ABL over land has a marked diurnal cycle during fair weather situations (Figure 4). During daytime, a mixed layer of vigorous turbulence grows in depth, typically capped by a statically stable inversion layer. The inversion layer also called entrainment zone is characterised by intermittent turbulence and overshooting thermals. The free atmosphere is entrained into the top of the boundary layer.

The entrainment zone is thinner when a stronger temperature inversion caps the boundary layer and thicker when higher turbulence and more active thermals are present. Near sunset, turbulence decays leave a weakly mixed residual layer in place of the mixed layer. At night, the bottom of the residual layer is transformed into a statically stable boundary layer. This **nocturnal boundary layer** is typically observed under clear sky conditions. Radiation to space cools the land surface, which therefore cools the adjacent air mainly through the process of molecular conduction and turbulence, and to a lesser extent through radiative transfer. The depth of the nocturnal boundary layer can grow up to a few hundreds of metres, depending on the season.
Figure 4: Theoretical diurnal evolution of the atmospheric boundary layer over land.

Figure 5 shows as an example the change in the mixing depth of the ABL during a day in the Los Angeles basin. Figure 5a shows the hazy layer of pollution in the morning hours. The same layer approximately doubles its depth in the late afternoon (Figure 5b).
Figure 5: Change in the mixing depth, Los Angeles, July 23, 2000 [Jacobson, 2002].
The ABL over the ocean (also called marine boundary layer (MBL)), in contrast to the ABL over land, is characterised by a nearly constant height throughout the day. The roughly constant temperature of the ocean surface (i.e. sea surface temperature (SST)) leads to a steady heat flux to the adjacent air parcels to the ocean surface. Therefore, no nocturnal boundary layer is built, and due to the constant SST the depth of the MBL is stable throughout a day.

The **mixed layer** in the ABL is characterised by a homogeneous mainly vertical distribution of quantities such as conservative tracers (i.e. trace gases with a longer lifetime than the transport process, absolute humidity, equivalent potential temperature, radioactivity, and CCN composition), and momentum or wind speed.

Turbulence within a mixed layer can be caused by either strong winds or wind shears that generate forced convection, or by free convection associated with large thermals. **Forced convection** is typically induced by mechanical forces such as deflection by a large-scale surface irregularity (i.e. buildings, mountains, waves, etc.). The mixed layers generated by **free convective** are typically caused by heating at the bottom boundary such as the Earth's surface or radiative cooling at the tops of cloud or fog layers.

Temperature inversions as the upper limit of the mixed layer of the ABL can be caused by different processes. The different notations used to describe temperature inversions are named according to their origin.

The **turbulence inversion** is built by strong turbulence within the surface layer, typically caused by strong winds. For example, starting with an initial condition of calm winds and a lapse rate of 6 K km\(^{-1}\), wind speed increases within the first 800 m, then air parcels start to move upwards and downwards, while their temperature changes dry adiabatically by 10 K km\(^{-1}\).

In the turbulence inversion the total heat energy of the mixed layer does not change. The average temperature also remains constant, therefore the resulting vertical temperature gradient of 10 K km\(^{-1}\) leads to a decrease in the temperature at the top of the mixed layer together with an increase in the temperature at its bottom. Consequently an inversion on top of the mixed layer is built.

Turbulence inversions are typically found in high pressure zones above the oceans, where strong trade winds are present. Furthermore, subsiding air in high
pressure systems leads to trade inversions, which enhance the building (or maintaining) of the temperature inversion.

The **subsidence inversion** is found in cases when large scale downward motion of air is observed, for example in high pressure systems. Starting from initial conditions with a vertical temperature gradient of 7 K km$^{-1}$ and no vertical movement of the air an air parcel starts descending for example 1 km above the height H and arrives at that height H 3 K warmer than its surrounding air having been consequently subjected to adiabatic warming. In Figure 6 the typical formation of a subsidence inversion is shown.

![Figure 6: Formation of a subsidence inversion](image)

The **trade inversion** is a specific form of the more general subsidence inversion. It is usually found in large-scale subsiding flows which constitute the descent branches of the Hadley cell and Walker circulation. This type of inversion is commonly found in trade-wind streams over the eastern portions of the tropical oceans.

The subsidence warming in the inversion layer is balanced by radiative cooling and evaporation from the tops of trade cumuli. The height of this inversion’s base varies from about 500 m at the eastern extremities of subtropical highs, to about 2000 m at the western and equatorial extremities. In the equatorial trough zone and over the western
portions of the trade-wind belt, the inversion does not exist as a mean condition, although it appears in certain weather patterns.

The strength of trade inversions varies enormously, occasionally being more than 10°C over 1 km, but sometimes being absent altogether, especially in the Northern Hemisphere. The inversion is generally strongest when the height of its base is lowest, and vice versa. The thickness of the inversion layer varies from only a few metres to more than 1000 metres. On the average its thickness is about 400 metres.

Airflow below a trade inversion is very moist and filled with cumulus clouds (trade cumuli). Above it, the air is warm and exceedingly dry; this structure is so characteristic of the trade current that tropical analysts think of the tropical troposphere as consisting of a lower moist and an upper dry layer [Riehl, 1954].

Overall, atmospheric conditions in general are typically a combination of several processes, and the air in the lower layers is vivid and also moves upwards and downwards. Therefore, air parcels in one layer sometimes subside much faster than in other layers leading to multiple temperature inversions.

Figure 7 shows how pollution is caped within two inversion layers in a certain height.
Figure 7: a) Smoke layer trapped in an inversion following a fire in Menlo Park, California (June, 2001), b) Elevated pollution layer (Los Angeles, July 22, 2000) [Jacobson, 2002].
Stability:

This study focuses on the static stability, therefore in the context of this thesis the word “stability” should be taken to mean “static stability” throughout. Knowledge about the stability of air parcels is essential to understand the possible influence of transport (i.e. horizontal and/or vertical) processes on the amounts of trace gases in different parts of the atmosphere. Many descriptions are given in the literature of how stability is defined in terms of temperature or energy.

The atmosphere is defined as being stable when a parcel of air which has been displaced vertically, returns to its original position. The atmosphere is unstable when a displaced air parcel continues to move in the same direction as it was when initially displaced. The atmosphere is neutral when a parcel remains still after being displaced.

These simple definitions lead to several different approaches to determining whether or not an atmosphere is stable. The most common approach is to take the potential temperature as the key indicator for stability. In general all the various approaches are self consistent, but there are differences in the cause and effect assumption [Stull, 1988, Jacob, 1999]. The main question that needs to be addressed is: Is the observed temperature profile the cause or the effect of the dynamical processes of the atmosphere?

The temperature profile is actually both the cause and the effect. This is because the actual temperature change of air with height (Environmental Lapse Rate ($\Gamma_E$)) as measured for example by radiosondes is only a snap-shot in time of the atmosphere. The actual temperature profile is dynamic and is continuously evolving. The environmental lapse rate plotted on a thermodynamic diagram is a snap shot in time of the atmosphere. The environmental lapse rate can be positive or negative and switch from one to the other with height. The average environment lapse rate is $6 \, \text{K} \, \text{km}^{-1}$. But this is just the average, and the lapse rate will always vary from this average.

Therefore, analyse of stability do not include the history of the investigated air, but it can state the future. However, the history of an air parcel can be determined by other long lived tracers such as potential vorticity, certain trace gas concentrations, etc.

Different temperatures are usually used to define the stability of the atmosphere. There are several sub divisions corresponding to different strengths of the atmosphere’s stability/instability, which are defined afterwards. The decision which temperature is useful to determine stability depends on whether clouds are present or not (i.e. does
condensation release latent heat or not) and on the amount of water vapour (i.e. is the amount of water vapour negligible for the density of an air parcel).

**Potential temperature** $\theta$ is the temperature of an unsaturated parcel of dry air brought adiabatically and reversibly from its initial state to a standard pressure, $p_0$, typically 1000 mbar.

$$\theta = T_0 \left( \frac{p_0}{p} \right)^{\kappa}$$  \hspace{1cm} (6)

$$\kappa = \frac{R_d}{c_{pd}} \frac{1 + r_v / \epsilon}{1 + r_v c_{pv} / c_{pd}} = 0.2854 \left( 1 - 0.24 r_v \right)$$ \hspace{1cm} (7)

where $\theta$ is the potential temperature, $T$ is the temperature, $\kappa$ (0.2854 for dry air) is the Poisson constant, $R_d$ and $c_{pd}$ are the gas constant and specific heat of dry air, $\epsilon$ is the ratio of the gas constant for water vapour and for dry air, $c_{pv}$ is the specific heat of water vapour, and $r_v$ is the water vapour mixing ratio.

**Equivalent temperature** is the temperature of an air parcel when all its water vapour condenses at constant pressure and the released energy is used to heat the air:

$$T_{ie} = T \left( 1 + \frac{L_w}{c_p T} \right)$$ \hspace{1cm} (8)

where $T_{ie}$ is the isobaric equivalent temperature, $T$ the temperature, $w$ the mixing ratio, $L$ the latent heat, and $c_p$ the specific heat of air at constant pressure.

**Adiabatic equivalent temperature** is the temperature that an air parcel has after undergoing a dry-adiabatic expansion until it is saturated, followed by a pseudoadiabatic expansion until all moisture is precipitated out, and finally brought back to the initial pressure with dry-adiabatic compression.

$$T_{ae} = T \exp \left( \frac{L_w}{c_p T} \right)$$ \hspace{1cm} (9)

being $T_{ae}$ the adiabatic equivalent temperature.

**Equivalent potential temperature** ($\theta_e$) is the temperature of an air parcel undergoing a dry-adiabatic expansion until it is saturated, followed by a pseudoadiabatic expansion until all moisture is precipitated out adiabatically and finally brought back to standard pressure with dry-adiabatic compression, $p_0$, typically 1000 mbar.
It is given most accurately as
\[
\theta_e = T \left( \frac{p_0}{p_d} \right)^{\frac{R_d}{c_{pd}}/\left(\frac{c_{pd}}{c} + \varepsilon\right)} r_{h}^{\frac{R_d}{c_{pd}}/\left(\frac{c_{pd}}{c} + \varepsilon\right)} \exp \left[ \frac{L_r r_v}{c_{pd} + r_c} T \right]
\]  \hspace{1cm} (10)

where \(\theta_e\) is the equivalent potential temperature, \(c_{pd}\) is the heat capacity at constant pressure of dry air, \(r_t\) is the total water mixing ratio, \(c\) is the heat capacity of liquid water, \(T\) is the temperature, \(R_d\) is the gas constant for dry air, \(p_d\) is the partial pressure of dry air, \(p_0\) is a reference pressure (usually 1000 mbar), \(L_v\) is the latent heat of vaporization, \(\varepsilon\) is the vapour mixing ratio, \(R\) is the gas constant for water vapor, and r.h. is the relative humidity [Paluch, 1979, Emanuel, 1994].

**Virtual temperature** is a fictitious temperature that takes into account moisture in the air. The formal definition of virtual temperature is the temperature that dry air would have if its pressure and specific volume were equal to those of a given sample of moist air. Virtual temperature allows meteorologists to use the equation of state for dry air even though moisture is present.

\[
\nu_T = T \left( \frac{1 + \frac{r_v}{\varepsilon}}{1 + r_v} \right)
\]  \hspace{1cm} (11)

where \(r_v\) is the mixing ratio, and \(\varepsilon\) is the ratio of the gas constants of air and water vapour, \(\approx 0.622\).

The stability of the atmosphere can be determined from the environmental lapse rate. Comparison with the dry and wet adiabatic lapse rates enables the estimation of the current stability. The temperatures above can be used to more easily investigate stability and to account for different processes occurring (i.e. condensation and/or density changes depending on the water content of the air parcel).

Any layer in the atmosphere is called **absolute stable**, if the environmental lapse rate decrease (or increase) with height is less than the cooling rate of the moist adiabatic lapse rate. The most stable layers are inversions where temperature increases with height.

The opposite, an **absolute unstable** atmosphere layer, is encountered where the environmental lapse rate decreases with height more than 9.8 K km\(^{-1}\) (rapid cooling with height).
Any layer defined as **conditional unstable** has an environmental lapse rate which decreases with height between the moist and dry adiabatic lapse rate. The air is unstable if saturated but stable if unsaturated. Saturated air cools less with height due to latent heat release thus allowing the parcel to be warmer than the environment if lifting occurs in a conditionally unstable environment.
Environmental lapse rate:

\[ \Gamma_E = -\frac{\Delta T}{\Delta z} \]  

(12)

Stability criteria for moist air:

- \( \Gamma_E > \Gamma_D \): absolute unstable
- \( \Gamma_E = \Gamma_D \): dry neutral
- \( \Gamma_D > \Gamma_E > \Gamma_W \): conditional unstable
- \( \Gamma_E = \Gamma_W \): wet neutral
- \( \Gamma_E < \Gamma_W \): absolute stable

Figure 8: Stability of air. Different regions of stability are marked by the black arrows. The red dotted line represents the dry adiabatic temperature profile \( (\Gamma_D) \), the blue dotted line is the wet adiabatic temperature profile \( (\Gamma_W) \), and the green lines show four possible environmental temperature profiles \( (\Gamma_E) \).
The level of free convection (LFC) is often found in the literature describing the level at which a parcel of air lifted dry-adiabatically until saturated and moist-adiabatically thereafter would first become warmer than its surroundings. This means that the parcel is now free to continue rising without the need of any additional energy input from the environment - hence it is "free" to continue convecting.

These preceding definitions are crucial elements in describing atmospheric dynamics.

Another important process involving horizontal transport of air masses is the sea (land) breeze. The same basic process can also be superimposed on, for example, large scale frontal systems arriving in coastal regions.

The sea (land) breeze is the notation for a horizontal process leading to a change of the vertical temperature profile. The process itself can be superimposed by for example large scale frontal systems arriving in coastal regions, however this process still takes place. Sea (and land) breezes are caused by unequal heating and cooling of adjacent land and sea surfaces. A sea breeze is wind with its direction from the sea to the land (and vice versa for the land breeze) in consequence of this differential heating.

The warmed air rises over the land surface, and a local circulation commences, with cool air from the sea being drawn in over the land. At the same time the ascending air returns seaward in what is known as the upper return current (Figure 9).
With weak general wind circulations (around the centre of a high for example), a sea breeze (pure sea breeze) moves over the coastline soon after the land temperature has exceed the sea temperature (late morning to early afternoon). As the difference increases, the sea breeze becomes stronger and extends farther inland. It also increases in depth from about 100 metre to as much as 450 to 800 metre in a well developed breeze. Maximum wind speed occurs a few hours after the maximum temperature is reached, generally during the mid to the late afternoon.

A weak sea breeze dies away soon after sunset, but a better developed sea breeze persists at the coast till 8 to 10 pm., usually dying away fairly suddenly at the coast and slowly moving seawards as a cut-off sea breeze circulation.

With stronger general wind circulations, coupled with the required temperature gradient, the development of the sea breeze becomes complicated. For example, a moderate to strong prevailing off-shore surface wind can delay the onset of the sea breeze. If strong enough, it can even prevent the sea breeze from developing at all. On-shore surface winds are generally enhanced by the sea breeze component.
2.1.2.2 Free atmosphere

The free atmosphere is commonly defined as the part of the atmosphere where the effect of the Earth's surface friction on air motion is negligible. The base of the free atmosphere usually taken as the point where the wind becomes geostrophic, or the top of the ABL.

2.1.2.3 Stratospheric/tropospheric exchange

The stratospheric/tropospheric exchange (STE) received attention in the early 1960’s when radioactive fallout from atmospheric nuclear test explosions became a major concern. The tropopause was expected to be impermeable at that time. However, the presence of different trace gases (e.g. H₂O, SO₂, CH₄, CO, etc.) within the stratosphere, which are primarily found in the troposphere, suggested that an upward flux towards the stratosphere of intruding anthropogenic and natural chemical constituents was occurring, which could therefore lead to global effects on the radiative balance and budget of different trace gases [Junge, 1962]. For example, the transport of chlorofluorocarbons into the stratosphere leads to O₃ destruction [Molina and Rowland, 1974].

Furthermore, the exchange between stratosphere and troposphere does not only occur in an upward direction. Conversely, the STE represents an important source of tropospheric O₃. This is achieved by entrainment from the stratosphere into the troposphere and contributes significantly to the removal of many other stratospheric species.

The intrusion of stratospheric air into the troposphere is largest where the Hadly cell meets the Ferrel cell, i.e. the border between the tropics and the extratropics (Figure 10).
The STE is pronounced as large latitudinal displacements occur. The shaded area in Figure 11 shows the region within the lower stratosphere most directly affected by these large scale motions. The STE mechanism is a cycle (Figure 11) in which tropospheric air at the inter tropospheric convergence zone (ITCZ) is lifted by cumulus convective turrets. The latent heat energy gained through condensation enables air parcels to penetrate into the stratosphere. Within the stratosphere the air of the lower tropical stratosphere is sucked by the extratropical stratosphere and transported towards the polar regions. Large scale subsidence and tropopause folding offers a thin band of stratospheric air the opportunity to enter into the troposphere along strongly tilted isentropes. Part of the stratospheric air in the fold returns reversibly to the stratosphere and part is drawn irreversibly into the troposphere [Holton et al., 1995]. Much of the O₃ transport from the lowermost stratosphere into the troposphere is believed to occur in connection with tropopause folding events.
Figure 11: Dynamical aspects of stratosphere–troposphere exchange. The tropopause is shown by the thick line. Thin lines are isentropic or constant potential temperature surfaces labelled in Kelvin. The heavily shaded region is the “lowermost stratosphere” where isentropic surfaces span the tropopause and isentropic exchange by tropopause folding occurs. The region above the 380 K surface is the “overworld”, in which isentropes lie entirely in the stratosphere. Light shading in the overworld denotes wave-induced forcing (the extratropical “pump”). The wiggly double headed arrows denote meridional transport by eddy motions, which include tropical upper-tropospheric troughs and their cut off cyclones as well as their midlatitude counterparts including folds. Not all eddy transports are shown; and the wiggly arrows are not meant to imply any two-way symmetry. The broad arrows show transport by the globalscale circulation, which is driven by the extratropical pump. This global-scale circulation is the primary contribution to exchange across isentropic surfaces (e.g. the ~380 K surface) that are entirely in the over world [Holton et al., 1995].
2.2 Chemistry of the troposphere

The Chapter focuses on the tropospheric photochemistry relevant for this study. In subsection (2.2.1) the “clean” atmosphere is described. The assumption of a nitrogen oxides (NO\textsubscript{x}) free troposphere, although hypothetical, is used to emphasize the dominant reactions in the marine boundary layer (MBL) and to illustrate the differences with the polluted atmosphere.

In the second subsection (2.2.2) the photochemical production of tropospheric ozone is outlined. This includes the discussion of the interaction of nitrogen oxide (NO) and nitrogen dioxide (NO\textsubscript{2}) with radicals, the oxidising steps of the NMHC, and the reactions of radicals and O\textsubscript{3}.

2.2.1 Chemistry of the clean marine troposphere

This chapter describes the chemistry of the “clean” (free of nitrogen oxides) boundary layer. As the chemistry of the troposphere is dominated by highly complex reaction chains, the reactions are thematically separated.

2.2.1.1 Hydroxyl radical (OH)

The photochemical reactions of ozone and the production of OH belong to the most important processes in the atmosphere. Ozone absorbs energy from the sunlight over a large spectral region. In the visible and ultraviolet spectral region the ozone molecule is photodissociated into an oxygen molecule and an oxygen atom. The photodissociation is here, for reasons of simplicity, divided into two different wavelength regions. In the first case the resultant oxygen atom is in the electronic ground state (O(\textsuperscript{3}P)) whereas in the second case the atom is in the first excited state (O(\textsuperscript{1}D)).

\[ O_3 + h\nu (\lambda < 420\text{nm}) \rightarrow O(\textsuperscript{3}P) + O_2 \]  
\[ O_3 + h\nu (\lambda < 320\text{nm}) \rightarrow O(\textsuperscript{1}D) + O_2 (\textsuperscript{1}\Delta) \]

In practice the O(\textsuperscript{3}P) atoms in the troposphere react completely with O\textsubscript{2} to form O\textsubscript{3}.

\[ O(\textsuperscript{3}P) + O_2 + M \rightarrow O_3 + M \]
The excited oxygen atoms ($O(^1D)$) are mainly quenched into the ground state ($^3P$) through collision with air molecules (M) (78% nitrogen ($N_2$); 21% oxygen ($O_2$)). The residue react with water ($H_2O$) to form hydroxy radicals (OH).

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2 \quad (16)$$

$$O(^1D) + O_2 \rightarrow O(^3P) + O_2 \quad (17)$$

$$O(^1D) + H_2O \rightarrow OH + OH \quad (18)$$

The rate of production of OH radicals depends on the relative rates of the reactions (16) (17), and (18). The branching ratio can be determined as follows:

$$\alpha_{(1,2,4),(2,5),(2,6)} = \frac{k_{(2,6)}[H_2O]}{k_{(2,6)}[H_2O] + k_{(2,4)}[N_2] + k_{(2,5)}[O_2]} \approx 7\mu[H_2O] \quad (19)^6$$

where $\mu[H_2O]=[H_2O]/[M]$, $H_2O$ is the vapour mixing ratio and M the total number of molecules per volume.

In the case of an atmospheric $H_2O$ mixing ratio of ~ 1% (which corresponds to 50% relative humidity (r.h.) at 20°C) around 10% of the $O(^1D)$ atoms react with $H_2O$ to form OH.

The significance of the OH radical in the chemical composition of the troposphere is caused by its high reactivity with nearly all gases that are emitted into the atmosphere by natural and/or anthropogenic activities.

For example, the reaction of OH with hydrocarbons, carbon monoxide (CO), the most abundant sulphuric and partially halogenated compounds, and nitrogen dioxide ($NO_2$) represents the most dominant loss process for these trace gases. As a consequence the lifetime of a large amount of trace gases is defined by their reactivity with OH.

This lifetime varies between a few hours for gases like e.g. isoprene ($C_5H_8$) or $NO_x$ (= NO + $NO_2$), to 1-2 months for CO and ~ 10 years for methane ($CH_4$). In the troposphere there are several trace gases that do not react with OH, like e.g. chloro

---

6 From the reactions (14) and (16)-(18), it is possible to estimate the average residence time of $O_3$ in the clean troposphere. The reaction of the $O(^1D)$ atoms with $H_2O$ (equation (19)) leads to a net $O_3$ destruction of 0.2 ozone molecules for every absorbed photon with a wavelength below 320 nm and maximum r.h. (i.e. $\mu[H_2O]=3\%$ under normal conditions). The half-life of $O_3$ is ~4 days considering a daily averaged photolysis frequency of $\tilde{j}(O(^1D))$ of $1\cdot10^{-5}$ s$^{-1}$ (middle latitude, summer). The photochemical lifetime in the free troposphere with significantly reduced $H_2O$ vapour mixing ratios increases to several weeks.
fluorocarbons (CFC₃, CF₂Cl₂) and N₂O, these gases can reach the stratosphere and disturb the chemistry there e.g., Molina and Rowland [1974].

2.2.1.2 Peroxy radicals (RO₂*)

**Production of RO₂***

The peroxy radicals \( RO_2^* = HO_2 + \sum R_i O_2 \) play a comparable role in the chemistry of the troposphere to the OH radical, although they are not as reactive. They achieve their importance in the MBL chemistry by destroying O₃. In addition, they are the key intermediates in the oxidation of long lived species and the production of peroxides and formaldehyde.

The production of RO₂* radicals takes place in the marine troposphere mainly via the oxidation of CO and CH₄ by the OH radical produced in reaction (18).

\[
OH + CO \rightarrow H + CO_2 \tag{20}
\]

\[
OH + CH_4 \rightarrow CH_3 + H_2O \tag{21}
\]

Around 60% of the OH radicals react in the unpolluted atmosphere with CO (90 ppbv, typical value in the remote northern hemisphere (NH)) and 40% with CH₄ (1,8 ppmv, average of the NH) [Gautrois et al., 1998]. In both reactions radicals are formed which react with O₂ to form RO₂* radicals.

\[
H + O_2 + M \rightarrow HO_2 + M \tag{22}
\]

\[
CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{23}
\]

---

7 The oxidation of CO with OH is one of the most important reactions in the tropospheric chemistry. The reaction shows some interesting kinetic features, which have to be taken into account, while developing a tropospheric model. First, the temperature dependence of the reaction differs significantly from the Arrhenius theory. The activation energy is close to zero at temperatures below 300 K. Secondly, the kinetic constant of the reaction is pressure dependent, and the reaction rate coefficient increases with increasing pressure. A possible explanation of this kinetical behaviour is the formation of a HOOCO complex in a discrete substep of the reaction:

\[
CO + OH \rightleftharpoons HOOCO \tag{a}
\]

\[
HOOCO \rightarrow H + CO_2 \tag{b}
\]

\[
HOOCO^* + M \rightleftharpoons HOOCO + M \tag{c}
\]

\[
HOOCO + O_2 \rightarrow HO_2 + CO_2 \tag{d}
\]

Reaction (c) followed by (d) leads to the possibility of a pressure dependent reaction path, which is not resulting into the products H + CO₂ from reaction (20). This reaction path takes place in the presence of O₂. The reaction (a) is favoured at low temperature, leading to a slightly negative temperature dependence of the reaction rate constant.
**Loss of RO₂⁺**

The RO₂⁺ are key intermediates in the photochemical processes generating peroxides (e.g. H₂O₂ and CH₃O₂H) and in the subsequent production of HCHO. The loss reactions of HO₂ and CH₃O₂ produce peroxides via reactions (24) and (25).

\[
\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \tag{24}
\]

\[
\text{HO}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O}_2\text{H} + \text{O}_2 \tag{25}
\]

The reactions (26), (27), and (28) are radical loss reactions of minor importance, since the CH₃O₂ self reactions (26) and (27) have reaction rate coefficients one order of magnitude smaller than the HO₂ self reaction. However, the CH₃O₂ concentration can be significantly higher than the concentration of HO₂, and consequently gain importance.

\[
\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{HCHO} + \text{CH}_3\text{OH} + \text{O}_2 \tag{26}
\]

\[
\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow 2 \cdot \text{CH}_3\text{O} + \text{O}_2 \tag{27}
\]

\[
\text{CH}_3\text{O}_2 + \text{OH} \rightarrow \text{CH}_3\text{OH} + \text{O}_2 \tag{28}
\]

The reaction pathways of radicals are highly complicated, and for simplicity only the most important pathways are shown. The methoxy radicals (CH₃O) and the hydroxymethyl radicals (CH₂OH) react with O₂ to form formaldehyde (HCHO) and HO₂ (see reactions (29) and (31)). The methanol (CH₃OH) can react with an OH radical (see reactions (30) and (31)) and therefore produce HCHO and HO₂.

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \tag{29}
\]

\[
\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH} \tag{30}
\]

\[
\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{HCHO} \tag{31}
\]

The peroxides are a reservoir for radicals when they photodissociate (see reactions (32) and (33)), this means that they are neutral referring to the radical balance (i.e. they produce radicals back). Net losses of radicals are caused by the reactions of the peroxides with OH (34), (35), and (36)). In these reactions are up to two radicals lost.

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow \text{OH} + \text{OH} \tag{32}
\]

\[
\text{CH}_3\text{O}_2\text{H} + \text{hv} \rightarrow \text{HCHO} + \text{H} + \text{OH} \tag{33}
\]

\[
\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O} \tag{34}
\]
The photolysis frequencies \( j(\text{H}_2\text{O}_2) \) and \( j(C\text{HO}_2\text{H}) \) are in the same order of magnitude as the reaction rate coefficients \( (k(34), (35), (36)) \) for the reaction with OH.

The dry and wet deposition rates of peroxides are high. This is especially true for the hydroperoxide being hydrophilic. The wash out of hydroperoxides is an important loss process for radicals in the troposphere.

### 2.2.1.3 Formaldehyde (HCHO)

Since the HCHO represents a similar reservoir substance as the peroxides, the HCHO reactions are of special interest for radicals. HCHO reacts with OH, decomposes, and photolyses in the same manner as the peroxides. The photolysis rate \( j(\text{HCHO}) \) is about one order of magnitude higher than the photolysis frequency of \( \text{H}_2\text{O}_2 \). The reaction rate coefficient of the reaction (37) of HCHO and OH is \( \sim 5 \) times higher than the respective value for the \( \text{H}_2\text{O}_2 \) reaction (34). The resultant lifetime of HCHO is one order of magnitude lower than the lifetime of \( \text{H}_2\text{O}_2 \) and amounts to a few hours during daytime.

\[
\text{HCHO} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O} \tag{37}
\]

\[
\text{HCHO} + \text{h} \nu \rightarrow \text{H}_2 + \text{CO} \tag{38}
\]

\[
\text{HCHO} + \text{h} \nu \rightarrow \text{H} + \text{CHO} \tag{39}
\]

The subsequent products of the oxidation and the photolysis of HCHO further react as follows:

\[
\text{CHO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO} \tag{40}
\]

\[
\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \tag{41}
\]

The photochemical processes of HCHO form radicals and can positively influence the radical balance (39).

---

8 The reaction (36) involves two steps: First an intermediate product CH\(_3\)OOH is formed, which under typical atmospheric conditions decomposes very rapidly into HCHO and OH.
2.2.1.4 Radical balance

Figure 12 shows the most important pathways of the radical reactions in the NO$_x$ free troposphere. Mechanisms leading to both recycling and net losses of radicals are represented.

Figure 12: O$_3$ loss and radical chemistry in a NOx free atmosphere. The Figure shows the radical balance of two initially produced OH radicals. The numbers in the boxes indicate the change of the number of free radicals [Schultz et al., 1996].
2.2.1.5 Ozone ($O_3$)

The analysis of ozone and radical loss processes in marine areas has recently received attention within the scientific community. High daytime $O_3$ losses have been observed over the ocean [Dickerson et al., 1999]. In the Indian Ocean e.g. $O_3$ losses of up to 50% and minimum $O_3$ mixing ratios around 5 ppbv in the MBL have been observed [Stehr et al., 2002]. There still remains considerable speculation about the processes possibly explaining the observations.

The dominant first order loss processes for $O_3$ during daytime are the photolysis, the dry deposition, and the reaction with OH and HO$_2$ (assuming NO$_x$, and halogen free conditions). When trying to determine the significance of these primary losses of $O_3$ it is assumed that the back reaction of O($^3P$) with O$_2$ proceeds instantaneously. This implies that the photolytical losses are equivalent to the production of OH through reaction (18).

$$O_3 + h\nu (\lambda < 320nm) \rightarrow O\left(^1D\right) + O_2$$  \hspace{1cm} (14)

Reverting to the radical balance (Figure 12) the reactions (42) and (43) are neutral, because the radicals interconvert themselves while transforming $O_3$ to $O_2$.

$$OH + O_3 \rightarrow HO_2 + O_2$$  \hspace{1cm} (42)
$$HO_2 + O_3 \rightarrow OH + 2\cdot O_2$$  \hspace{1cm} (43)

The reaction chain is only terminated by radical-radical reactions. The following loss reactions are dominant for the HO$_x$ cycle under NO$_x$ free atmospheric conditions:

$$OH + OH \rightarrow H_2O + O\left(^3P\right)$$  \hspace{1cm} (44)
$$OH + OH \rightarrow H_2O_2$$  \hspace{1cm} (45)
$$OH + HO_2 \rightarrow H_2O + O_2$$  \hspace{1cm} (46)
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$  \hspace{1cm} (47)

From the above mentioned reactions the net balance equation for $O_3$ related to HO$_x$ results:
Cycle A:

\begin{align*}
o_3 + ln \left( \lambda < 420nm \right) & \rightarrow O\left(^3P\right) + O_2 \\
o\left(^1D\right) + N_2 & \rightarrow O\left(^3P\right) + N_2 \\
o\left(^1D\right) + O_2 & \rightarrow O\left(^3P\right) + O_2 \\
3 \cdot \left(o\left(^3P\right) + O_2 + M \rightarrow O_3 + M \right) & \\
2 \cdot \left(HO_2 + O_3 \rightarrow OH + 2 \cdot O_2 \right) & \\
2 \cdot \left(OH + O_3 \rightarrow HO_2 + O_2 \right) & \\
2 \cdot \left(OH + CO \rightarrow H + CO_2 \right) & \\
2 \cdot \left(H + O_2 + M \rightarrow HO_2 + M \right) & \\
3 \cdot \left(o_3 + ln \left( \lambda < 320nm \right) \rightarrow O\left(^1D\right) + O_2 \right) & \\
\end{align*}

net: \hspace{1cm} 3 \cdot O_3 + CO \rightarrow 4 \cdot O_2 + CO_2

Cycle A has a negative effect on the O₃ balance, three O₃ molecules and one CO molecule are converted into four O₂ molecules and one CO₂ molecule.

2.2.1.6 Methane (CH₄)

The variety of possible reaction pathways for the oxydation of methane clearly shows the complexity of the chemistry even in remote unpolluted areas. Each possible reaction pathway, starting from the top of Figure 13 to the bottom describes the influence on the O₃ and radical balance. It is difficult to identify which pathway is predominant because the absolute reaction rates varying throughout the day.
2.2.1.7 Non methane hydrocabs (NMHC)

In the chemistry of the remote MBL the oxidation of the NMHC can in a first approximation be considered as negligible. In spite of their partially higher reactivity, the NMHC have no important influence on the chemistry because their concentrations are significantly lower than the concentrations of CH\textsubscript{4} [Rudolph and Johnen, 1990]. The discussion of the reactions involving NMHC has been deferred to chapter 2.2.2 focusing on the chemistry of polluted atmospheres, where they play an important role.

2.2.1.8 Halogens (Br, Cl, I)

Several hypothesis regarding the possible noticeable influence of halogens on the photochemistry of the MBL have been reported in the literature [e.g. Keene et al., 1990, Pszenny et al., 1993, Fan and Jacob, 1992, Finlayson-Pitts, 1993, Parrish et al., 1993, McKeen and Liu, 1993, Graedel and Keene, 1995, Keene et al., 1996, Ariya et al., 1998].

Vogt et al. [1996], Sander and Crutzen [1996], and Sander et al. [1997] have concluded from observations of O\textsubscript{3} losses, which cannot be explained by the known chemistry, that another loss cycle is needed. The cycle should not involve high NO\textsubscript{x} concentrations, because the O\textsubscript{3} losses have been observed in remote regions without anthropogenic sources.
They proposed a cycle removing O$_3$ as follows:

\[
\begin{align*}
Br + O_3 & \rightarrow BrO + O_2 \\
BrO + HO_2 & \rightarrow HOBr + O_2 \\
HOBr + h\nu & \rightarrow OH + Br
\end{align*}
\]

net:

\[O_3 + HO_2 \rightarrow OH + 2 \cdot O_2\]

In recent laboratory experiments the formation of Br$_2$ through the reaction of sodium bromide (NaBr) particles was reported by Hirokawa et al. [1998]. Spicer et al. [1998] observed relevant amounts of Cl$_2$ and Br$_2$ during the night, however there still remain large uncertainties over the origin and the whereabouts of the tropospheric halogens.

One possibility for the origin of Br was postulated by Vogt et al. [1996]. They propose an auto catalytic mechanism for the emission of halogens from sea salt aerosols into the gas phase. The mechanism is initiated by the adsorption of HOBr in the gas phase on aerosols, which is then converted into hydrophobic BrCl and Br$_2$ (Figure 14). Afterwards the BrCl and Br$_2$ turn into the gaseous phase.

\[
\begin{align*}
HOBr + Cl^- + H^+ & \rightleftharpoons BrCl + H_2O \\
BrCl + Br^- & \rightleftharpoons Br_2Cl^- \\
Br_2Cl^- & \rightleftharpoons Br_2 + Cl^- \\
Br_2 + h\nu & \rightarrow 2Br \\
2 \cdot (Br + O_3 & \rightarrow BrO + O_2) \\
2 \cdot (BrO + HO_2 & \rightarrow HOBr + O_2)
\end{align*}
\]

net:

\[2HO_2 + H^+ + 2O_3 + Br^- + h\nu \rightarrow HOBr + 4O_2 + H_2O\]
The most recent atmospheric models reveal that larger amounts of Cl radicals are unlikely, because their presence would reduce the hydrocarbon concentrations to levels unrealistically low [Finlayson-Pitts, 1993, Parrish et al., 1993, McKeen and Liu, 1993, Graedel and Keene, 1995, Wingenter et al., 1996]. Conversely, the observed amounts of HCHO [Wagner et al., 2001, 2002], the observed isotopic fractionation of CH₄ [Allan et al., 2001], and the diurnal evolution of the RO₂⁺ concentration [Burkert et al., 2003a] suggest that the presence of low amounts of Cl are responsible for the differences between measurements and calculations.

The presence of both chlorine and bromine is predicted to come from sea salt aerosols by the MOCCA model [Sander and Crutzen, 1996, Dickerson et al., 1999, Vogt et al., 1996]. Others have speculated that Cl can be generated from sea salt particles in the presence of sufficient amounts of NO₂, N₂O₅ or CIONO₂ with reactions (57) and (58) [Finlayson-Pitts, 1993, Graedel and Keene, 1995, Vogt et al., 1996].

Figure 14: A simplified scheme of the bromine cycling between homogeneous and heterogeneous phase [Color image adapted from Sander and Crutzen, 1996].
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\[
2NO_2(s) + NaCl(s) \rightarrow ClNO_2(s) + NaNO_3(s) \tag{55}
\]

\[
2NO_2(s) + NaBr(s) \rightarrow BrNO_2(s) + NaNO_3(s) \tag{56}
\]

\[
N_2O_5(s) + NaCl(s) \rightarrow ClNO_2(s) + NaNO_3(s) \tag{57}
\]

\[
ClONO_2(s) + NaCl(s) \rightarrow Cl_2(s) + NaNO_3(s) \tag{58}
\]

Photolysis then generates chlorine atoms, e.g.

\[
ClNO_2 + h\nu \rightarrow Cl + NO_2 \tag{59}
\]

\[
Cl_2 + h\nu \rightarrow 2Cl \tag{60}
\]

An alternative potential explanation for the presence of significant amounts of Cl in the atmosphere is by the enhanced emissions of halogenated carbon compounds such as CH$_3$Cl in coastal regions. The Cl is produced through the following oxidation pathways.

\[
CH_3Cl + OH \rightarrow CH_2Cl + H_2O \tag{61}
\]

\[
CH_2Cl + O_2 + M \rightarrow CH_2ClO_2 + M \tag{62}
\]

\[
CH_2ClO_2 + NO \rightarrow CH_2ClO + NO_2 \tag{63}
\]

\[
CH_2ClO + O_2 \rightarrow CHOCl + HO_2 \tag{64}
\]

\[
CH_2ClO_2 + HO_2 \rightarrow CH_2ClOOH + O_2 \tag{65}
\]

\[
CH_2ClO_2 + RO_2 \rightarrow CH_2ClO + RO + O_2 \tag{66}
\]

\[
CH_2ClO_2 + RO_2 \rightarrow CHOCl + ROH + O_2 \tag{67}
\]

\[
CH_2ClO_2 + RO_2 \rightarrow CH_2ClOOH + R' \left( R' = R_{H-1} \right) O + O_2 \tag{68}
\]

\[
CH_2ClOOH + OH \rightarrow CH_2ClO_2 + H_2O \tag{69}
\]

\[
CH_2ClOOH + OH \rightarrow CHOCl + OH + H_2O \tag{70}
\]

\[
CH_2ClOOH + h\nu \rightarrow CH_2ClO + OH \tag{71}
\]

\[
CHOCl + OH \rightarrow CO + Cl + H_2O \tag{72}
\]

\[
CHOCl + h\nu \rightarrow CO + Cl + H \tag{73}
\]

\[
CH_2ClOH + OH + O_2 \rightarrow CHOCl + HO_2 + H_2O \tag{74}
\]

Several studies [Khalil and Rasmussen, 1999, Moore et al., 1996] have shown that the ocean is not a significant source CH$_3$Cl. However, Yokouchi et al. [2000]
observed up to 2100 pptv of CH$_2$Cl on islands in the tropics, but these high mixing ratios might be related to emissions from forested land.

Cl reacts in the same way as Br with O$_3$ and leads through its catalytic cycle to a net loss of O$_3$. In addition, the reaction rate coefficient of Cl with O$_3$ is one order of magnitude higher compared to the equivalent for Br.

The **iodine (I)** halogen is supposed to be dominantly emitted via biological activities as a hydrocarbon complex [Cicerone, 1981, Rasmussen et al., 1982, Singh et al., 1983, Class and Ballschmiter, 1988, Carlier et al., 1991, Reifenhäuser and Heumann, 1992, Schall and Heumann, 1993, Carpenter et al., 1998]. The emission is strongly dependent on the tide and therefore higher amounts of I are expected in coastal regions [Carpenter et al., 1999, 2000]. By contrast to Br and Cl halogens, I is supposed not to be produced by heterogeneous chemistry on aerosols. However, Vogt et al. [1999] suggested that I compounds partly go into the aqueous phase, but are cycled back. There remain many unknowns about the reactions and sources producing I atoms. However, I contributes to the loss of O$_3$. Three catalytic cycles are proposed, first by Chameides and Davis [1980] for low I concentrations.

**Cycle 1:**

\[ I + O_3 \rightarrow IO + O_2 \]  
(75)

\[ IO + HO_2 \rightarrow HOI + O_2 \]  
(76)

\[ HOI + h\nu \rightarrow OH + I \]  
(77)

net:

\[ O_3 + HO_2 \rightarrow OH + 2 \cdot O_2 \]  

The IO self reaction becomes more important at higher iodine concentrations and the reaction cycle changes [Chameides and Davis, 1980, Chatfield and Crutzen, 1990, Jenkin, 1992].

**Cycle 2:**

\[ 2(I + O_3) \rightarrow 2(IO + O_2) \]  
(75)

\[ IO + IO \rightarrow 2I + O_2 \]  
(78)

\[ IO + IO \rightarrow I_2O_2 \]  
(79)

\[ I_2O_2 + h\nu \rightarrow 2I + O_2 \]  
(80)

net:

\[ 2O_3 \rightarrow 3O_2 \]
The third catalytic cycle suggested by Solomon et al. [1994] needs higher amounts of BrO to recycle IO.

Cycle 3:

\[
\begin{align*}
I + O_3 & \rightarrow IO + O_2 \quad (75) \\
BrO + O_3 & \rightarrow BrO + O_2 \quad (48) \\
BrO + IO & \rightarrow Br + I + O_2 \\
\text{net:} & \quad 2O_3 \rightarrow 3O_2
\end{align*}
\]

### 2.2.1.9 Influence of halogens and radicals on the O\(_3\) balance

Considering the above mentioned reaction paths, the chemical and photolytical reactions lead to a depletion of O\(_3\) in the NO\(_x\) free atmosphere. Exemplary, the case of Br is considered, the loss processes by Cl and I can be treated in the same way.

The temporal variation of O\(_3\) can be calculated with equation (82).

\[
\frac{d[O_3]}{dt} = k_{(2,3)} [O(\text{^3}P)][O_3] - k_{(2,12)} [HO_2][O_3] - k_{(2,11)} [OH][O_3]
- k_{(2,33)} [Br][O_3] - j(O(\text{^3}D))[O_3] - j(O(\text{^1}P))[O_3] \\
(82)
\]

Assuming that reaction (15) proceeds instantaneously the equation (82) can be approximated to

\[
\frac{d[O_3]}{dt} = -k_{(2,12)} [HO_2][O_3] - k_{(2,11)} [OH][O_3] - k_{(2,34)} [Br][O_3] - \alpha_{(2,4),(2,5),(2,6)} \cdot j(O(\text{^3}D))[O_3].
\]

Another loss process for O\(_3\) not yet quantified is the dry and wet deposition on surfaces, see Ganzeveld and Lelieveld [1995].

The importance of the different loss processes of O\(_3\) is illustrated in chapter 4.3.3.1, where losses of relevant trace gases are quantified.
2.2.2 Chemistry of the polluted troposphere

In contrast to the chemistry of the marine troposphere, described in chapter 2.2.1, reactions involving nitrogen oxides are of great relevance in polluted atmospheres (i.e. NO\textsubscript{x} > 40pptv). These reactions lead to O\textsubscript{3} production and are responsible for the formation of e.g. nitrates. Under special topographical and meteorological circumstances the O\textsubscript{3} mixing ratios can reach extremely high values in the lower troposphere. The first evidence was found while investigating the summer smog phenomena in Los Angeles [Haagen-Smit, 1952, Cadle and Johnston, 1952].

2.2.2.1 Nitrogen oxides (NO, NO\textsubscript{2})

The reactive molecules NO and NO\textsubscript{2} play a key role in the photochemistry of O\textsubscript{3}. The main source of NO\textsubscript{x} (=NO+NO\textsubscript{2}) in the troposphere is anthropogenic (~80%) [Müller, 1992], with 20% originating naturally from plants, surface emissions, and from lightning [Dickerson, 1984, Galbally et al., 1985, Kaplan et al., 1988, Williams et al., 1992].

Nitrogen oxide emissions consist mainly (>90%) of NO, especially in urban areas with high traffic events („rush hours“) with high concentrations of NO\textsubscript{x} being observed in the early morning. The NO reacts rapidly with O\textsubscript{3} to form NO\textsubscript{2}. Therefore high NO concentrations are accompanied with high NO\textsubscript{2} concentrations, when sufficient amounts of O\textsubscript{3} are present.

\[
NO + O_3 \rightarrow NO_2 + O_2 \tag{83}
\]

The lifetime \(\tau\) of NO can be calculated in a first approach from the reaction rate coefficient for reaction (83) and an O\textsubscript{3} mixing ratio. A typical mixing ratio for the polluted lower troposphere is 60 ppbv leads to \(\tau \sim 34\text{s}\).

\[
\tau = \frac{1}{k_{(2.43)}[O_3]},
\]

During the night the reaction (83) represents a net sink for O\textsubscript{3}, because the subsequent reactions (described in chapter 2.2.2.2), are the initiators for the so called "nighttime chemistry" and they lead to additional losses of the produced NO\textsubscript{2}. This is in contrast to the NO\textsubscript{2} produced during the day, which is immediately photodissociated to form a NO molecule back. In addition an O atom in the electronical ground state (\(^3\text{P}\)) is produced, reacting together with O\textsubscript{2} back to form an O\textsubscript{3} molecule (15).
\[ NO_2 + h\nu (315\text{nm} < \lambda < 420\text{nm}) \rightarrow NO + O( ^3P) \]  
\[ O( ^3P) + O_2 + M \rightarrow O_3 + M \]

2.2.2.1 Photostationary state (PSS)

The photolysis frequency \( j_{(NO_2)} \) from reaction (84) reaches values up to \( 1 \times 10^{-2} \text{s}^{-1} \) (i.e. at noon, during summer, at the surface, in middle latitudes). The absolute rate for reaction (84) is in that case of the same order of magnitude as for reaction (83). According to these reactions between NO and NO\(_2\) a quasi stationary equilibrium (PSS = photostationary state) is achieved within 1 to 2 minutes. Assuming the PSS for the involved species,

\[
\frac{d[O_3]}{dt} = \frac{d[NO_2]}{dt} = \frac{d[NO]}{dt} = \frac{d[O(^3P)]}{dt} = 0
\]

results in

\[ j_{(NO_2)}[NO_2] - k_{(83)}[NO][O_3] = 0. \]  
(85)

Cycle C:

\[ NO + O_3 \rightarrow NO_2 + O_2 \]  
(83)

\[ O(^3P) + O_2 + M \rightarrow O_3 + M \]  
(15)

\[ NO_2 + h\nu (315\text{nm} < \lambda < 420\text{nm}) \rightarrow NO + O( ^3P) \]  
(84)

net:

\[ 0 \rightarrow 0 \]

The net equation from cycle C reveals that within this cycle no net O\(_3\) is produced, only the PSS between NO and NO\(_2\) is achieved [Leighton, 1961].

The equation (85) assumes that all other reactions are of minor importance. However, the absolute reaction rates (i.e. the total amount of molecules cm\(^{-3}\) s\(^{-1}\) produced by a reaction, e.g. \( k_{A+B}[A][B] \)) of the peroxy radicals with NO are in comparison slow, but they have an important impact. They disturb the PSS between NO, NO\(_2\) and O\(_3\) leading therefore to a higher amount of O\(_3\) than in the undisturbed case.

NO is oxidised with the peroxy radicals via the following reactions,

\[ NO + HO_2 \rightarrow NO_2 + OH \]  
(86)

\[ NO + RO_2 \rightarrow NO_2 + RO. \]  
(87)
The additional amount of NO\(_2\) produced leads to a net production of O\(_3\) via reaction (84) and the subsequent reaction (15), where R represents the corresponding hydrocarbon group. During daytime conditions the reactions (86) and (87) are rate determining for the O\(_3\) production rate, and to a good approximation the following reaction can be applied (for the derivation of this equation see Appendix 0).

\[
\frac{d[O_3]}{dt} = [NO] \left( \sum_i \left( k_i \cdot [RO_2] \right) + k_{(2.45)} \cdot [HO_2] \right)
\]  (88)

The index i represents the different hydrocarbon groups. In principle they all react at different velocities with NO. The kinetic investigations of peroxy radical reactions with NO, however, have revealed large discrepancies in the last decade. In the past, it was assumed that all the peroxy radicals react at the same velocity with NO [e.g. Finlayson-Pitts and Pitts, 1986, and references therein]. In recent years several authors have revised this assumption [e.g. Kirchner et al., 1990, Moortgard et al., 1989, Peeters et al., 1992, Sehested and Nielsen, 1993, Le Bras et al., 1994]. However, the most recent investigations [Eberhard and Howard, 1997] confirmed that the C3-C5 and to a large extent also the larger peroxy radicals react at the same velocity with NO. Thus, an average reaction rate coefficient for reaction ((86) und (87)) of 

\[ k_{\text{average}} = 8 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s} \]  

can be assumed. With this and the simultaneous knowledge of O\(_3\), NO, NO\(_2\), and \( j_{(NO_2)} \), the total concentration of all peroxy radicals can be calculated:

\[
RO_2^{pss} = RO_2^{pss} + HO_2^{pss} = \frac{j_{(NO_2)}}{k_{\text{average}}} \cdot \frac{NO_2}{NO} - \frac{k_{(2.43)}}{k_{\text{average}}} \cdot [O_3]
\]

### 2.2.2.1.2 Nitrogen oxides in the ozone balance

As described in cycle C (see section 2.2.2.1.1), there is no net production of O\(_3\) from the reactions (15), (83), and (84). The presence of peroxy radicals as shown in equation (88) leads to a net production of O\(_3\). The formed NO\(_2\) molecules from the reactions (86) and (87) are not produced by the destruction of an O\(_3\) molecule. The O\(_3\) production goes into competition with the reactions (42), (43), and (14) (chapter 2.2.1). Whereat the O(^1D) atoms formed by reaction (14) mainly relaxate by quenching (reaction (16) and (17)) into the ground state and form back O\(_3\) via reaction (15). The net loss is only caused by the O(^1D) atoms leading to the formation of OH. This part is represented by the factor \( \alpha_{(2.4),(2.5),(2.6)} \) (section 2.2.1.1).
The extent of \( \text{O}_3 \) production depends on the amount of NO\(_x\) present. Lightfoot et al. [1992] calculated a NO\(_x\) mixing ratio threshold of 40 pptv (assuming 20 ppbv \( \text{O}_3 \)), by which \( \text{O}_3 \) is neither produced nor destroyed. If assuming a PSS for NO\(_2\), \( \text{O}_3\), O\(^{(3)}\text{P}\), and O\(^{(1)}\text{D}\) the reactions (13)-(18), (42), (43), (86), and (87) provide the time dependent variation of the \( \text{O}_3 \) concentration.

\[
\frac{\partial[\text{O}_3]}{\partial t} = k_{\text{average}} \cdot [\text{NO}] \cdot [\text{RO}_2^*] - \alpha_{(2.4),(2.5),(2.6)} \cdot j_{(\text{O}^{(1)}\text{D})} [\text{O}_3]
\]

\[
- k_{(2.12)} \cdot [\text{HO}_2] [\text{O}_3] - k_{(2.11)} \cdot [\text{OH}] [\text{O}_3]
\]

The threshold value for NO at which a net \( \text{O}_3 \) production starts can be calculated by a simple transformation.

\[
[\text{NO}] > \frac{\alpha_{(2.4),(2.5),(2.6)} \cdot j_{(\text{O}^{(1)}\text{D})} [\text{O}_3] + k_{(2.12)} \cdot [\text{HO}_2] [\text{O}_3] + k_{(2.11)} \cdot [\text{OH}] [\text{O}_3]}{k_{\text{average}} \cdot [\text{RO}_2^*]}
\]

If typical values for \( \alpha_{(2.4),(2.5),(2.6)} = 7 \mu\text{mol(H}_2\text{O)}, \mu\text{mol(H}_2\text{O)} (1\%), j_{(\text{O}^{(1)}\text{D})} = (3.2 \cdot 10^5 \text{s}^{-1}) \), \( \text{O}_3 \) (40 ppbv), \( \text{HO}_2 \) (20 pptv), and \( \text{CH}_3\text{O}_2 \) (20 pptv) are considered the NO mixing ratio of 20 pptv represents the threshold NO value.

The ratio between NO\(_2\) and NO, necessary for the calculation of the NO\(_x\) mixing ratio, can be estimated from the simple PSS (of reactions (15), (83), and (84)).

\[
\frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_{(2.43)} [\text{O}_3]}{j_{(\text{NO}_2)}}
\]

Assuming a typical photolysis rate for mid latitudes for NO\(_2\) of \( j_{(\text{NO}_2)} = 0.01 \text{s}^{-1} \) a NO\(_2\)/NO ratio of ~2 results, implying NO\(_x\) ~ 40 pptv. The amount of NO\(_x\) depends on the \( \text{O}_3 \), \( \text{H}_2\text{O} \) vapour concentration and photolysis frequencies.

### 2.2.2.1.3 Loss processes of nitrogen oxides

Nitrogen oxides are predominantly removed by the reactions involving NO\(_2\) and the subsequent wet and dry deposition of the products. For NO\(_2\), only reactions with some organic peroxy radicals (see chapter 2.2.2.2) can compete with the fast photochemical cycle (83) - (87). The share of nitrate production to the total turnover is below 30% for the most radicals [Becker and Wirtz, 1989, Roberts, 1990].

Main loss processes are the following:

- The reaction of NO\(_2\) with OH during the day represents the most dominant loss for NO\(_x\).
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\[ \text{NO}_2 + \text{OH} + M \rightarrow \text{HNO}_3 + M \quad (89) \]

The nitric acid (HNO\(_3\)) formed in reaction (89) is highly water soluble and reacts rapidly with surfaces (dry deposition). Therefore, HNO\(_3\) can easily be washed out or deposed from the atmosphere.

- NO\(_2\) reacts with HO\(_2\) or organic peroxy radicals (RO\(_2\)), in both cases the formed peroxy nitrates are thermal unstable and frequently decompose within a short period of time back to the educts.

\[
\begin{align*}
\text{NO}_2 + \text{HO}_2 & \rightleftharpoons \text{HO}_2\text{NO}_2 \quad (90) \\
\text{NO}_2 + \text{RO}_2 & \rightleftharpoons \text{RO}_2\text{NO}_2 \quad (91)
\end{align*}
\]

The hydroperoxy nitrate (HO\(_2\)NO\(_2\)) and the alkylperoxy nitrates (RO\(_2\)NO\(_2\)) formed via alkylperoxy radicals (e.g. CH\(_3\)O\(_2\), C\(_2\)H\(_5\)O\(_2\), ...) which typically react with NO\(_2\) in the lower troposphere have only a lifetime of a few seconds. In contrast to the peroxy acetyl nitrates (PAN), due to their essential higher activation energy, which can have lifetimes up to several months at lower temperatures, when it is transported into the free troposphere. PAN as a reservoir for NO\(_x\) can therefore have a significant influence on the local amounts of reactive nitrogen oxides, even in unpolluted regions [Singh et al., 1990, 1992]. The formation reactions (90) and (91) of organic nitrates are not a sink for the total amount of NO\(_x\), because the deposition velocities are very low compared with the thermal decomposition.

- In layers close to the surface the dry deposition of NO\(_2\) is important. The deposition velocities vary between 0.2 and 0.4 cm s\(^{-1}\) [Hanson and Lindberg, 1991].

- The reaction with O\(_3\) constitutes an additional NO\(_2\) loss mechanism.

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad (92) \]

The formed NO\(_3\) radical is very rapidly photodissociated during daytime into NO or NO\(_2\) (see reaction (93)). The nocturnal chemistry is described in more detail in section 2.2.2.2.
2.2.2.2 Nitrate radical (NO₃)

The NO₃ radical, produced within reaction (92), plays an important role during the night. During daytime it is rapidly photodissociated being the amounts of NO₃ negligible.

\[
NO_3 + h\nu \xrightarrow{a} NO_2 + O\left( ^3P \right) \xrightarrow{b} NO + O_2
\]  

(93)

NO₃ is produced by the dissociation of N₂O₅.

\[
NO_2 + NO_3 + M \rightarrow N_2O_5 + M
\]  

(94)

\[
N_2O_5 + M \rightarrow NO_3 + NO_2 + M
\]  

(95)

N₂O₅ is a reservoir substance not a net source, because N₂O₅ is exclusively produced by reaction (94) [Wayne et al., 1990].

The NO₃ radical oxidises several organic compounds present in the troposphere. During daytime the OH radical is the dominant reaction partner for the oxidation of organic compounds. Conversely, during the night the NO₃ radical is for almost all organic compounds the most important oxidising agent in the troposphere. For a few compounds, e.g. CH₃SCH₃, the reaction with NO₃ during the night can be even more significant than the daytime reaction with OH.

The rate coefficients for the reaction of hydrocarbons with NO₃ are clearly smaller than the corresponding reaction rate coefficients with OH. For instance, the relative reactivity of OH with hydrocarbons for example for butane and 1-butene are in the order of 10⁵ and 3000 respectively higher than the corresponding for NO₃ at temperatures around 20°C. The importance of the separate pathways is emphasized when the concentrations of NO₃ during the night (~10⁹ molecules cm⁻³) and of OH during the day (~10⁶ molecules cm⁻³) are taken into account. The absolute reaction rates of NO₃ with alkenes during the night are of the same order of magnitude compared with the rates of OH during the day.

Terpenes have comparatively much higher reaction rate coefficients with NO₃. The rate coefficients are only two orders of magnitude smaller than the corresponding for OH. In this case the reactions of natural terpenes with NO₃ during the night can be more significant than with OH during daytime.

---

9 The part of channel a to reaction (93) amount to ~ 90%.
Two typical reaction mechanisms can be identified: the hydrogen abstraction
and the addition to an unsaturated bonding.

\[ \text{NO}_3 + RH \rightarrow \text{HNO}_3 + R \]  \hspace{1cm} (96)

\[ \text{NO}_3 + C_2H_4 \rightarrow C_2H_4\text{ONO}_2 \]  \hspace{1cm} (97)

\( \text{HNO}_3 \) is a direct product of the hydrogen abstraction of the \( \text{NO}_3 \) radical. The
produced R radical in reaction (96) reacts predominantly with \( \text{O}_2 \) to form \( \text{RO}_2^* \) in the
troposphere. The other aldehyde precursors produce an acyl peroxy radical \( (\text{RCOO}_2) \) as
a product of reaction (96) and therefore are a potential source for PAN.

The product from reaction (97) can be a \( \text{NO}_2 \) sink, because of its reaction with
\( \text{NO}_2 \) producing epoxides. However, in the troposphere the reaction with \( \text{O}_2 \) dominates.
For example propene reacts with \( \text{O}_2 \):

\[ \text{CH}_3\text{CHCH}_2\text{ONO}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{CHOOCCH}_2\text{ONO}_2 \]  \hspace{1cm} (98)

and produces nitrated acetone by reactions (99) and (100).

\[ \text{CH}_3\text{CHOOCCH}_2\text{ONO}_2 + \text{NO} \rightarrow \text{CH}_3\text{CHOCH}_2\text{ONO}_2 + \text{NO}_2 \]  \hspace{1cm} (99)

\[ \text{CH}_3\text{CHOCH}_2\text{ONO}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{ONO}_2 + \text{HO}_2 \]  \hspace{1cm} (100)

These reactions underline, the analogy to the reaction (87) and (106). They
constitute a source of \( \text{HO}_2 \) radicals during the night enabling the conversion of \( \text{NO} \) to
\( \text{NO}_2 \).

Of special interest is the production of \( \alpha-\text{(nitroxy)}\)-acetone, reported as a
mutagen. Other products are di-nitrates which also have noxious reactions.

The role of \( \text{NO}_3 \) in the tropospheric chemistry can be summarised as follows:

- Organic compounds can be oxidised and removed from the atmosphere during the
  night.
- \( \text{HNO}_3 \) can be produced, either by the hydrolysis of \( \text{N}_2\text{O}_5 \) or as a product of the H
  abstraction from reaction (96).
- Free radicals from the reaction of \( \text{NO}_3 \) with organic compounds can rapidly be
  converted into \( \text{HO}_2 \) und \( \text{RO}_2 \), and therefore initiate oxidising chain reactions, which
  lead to a source of OH radicals.
- Toxic compounds, other nitrates, and oxidised compounds can be formed.
2.2.2.3 Nitrous acid (HONO)

HONO is of great interest because of its absorption of light in the actinic region and rapid photolysis to generate OH radicals ((101)).

\[ \text{HONO} + h\nu \rightarrow \text{OH} + \text{NO} \]  \hspace{1cm} (101)

This reaction can have a major impact on the production of OH especially in the early morning hours, because HONO is mainly produced and accumulated during the night by heterogeneous reactions of NO₂. During the day it can also be formed by the reaction of OH with NO:

\[ \text{OH} + \text{NO} + M \rightarrow \text{HONO} + M \]  \hspace{1cm} (102)

Winer and Biermann [1994] observed HONO mixing ratios up to 15 ppbv in the early morning hours at Long Beach, California. However, the impact of these two reactions on the production of radicals during daytime can be neglected.

2.2.2.4 Non methane hydrocarbons (NMHC)

2.2.2.4.1 OH oxidation of NMHC

The oxidation of NMHC in polluted regions plays a significant role among the production of RO₂⁺ radicals. The NMHC are a large group of different substances which have both anthropogenic and natural origin (Figure 15).

![Figure 15: Different groups of volatile organic compounds found in the Earth’s atmosphere, with typical examples for each group.](image-url)
In order to keep the discussion at a reasonable degree of complexity only reactions with OH as initialising step are included (the NO$_3$, O$_3$, and Cl oxidation is described in chapters 2.2.2.2, 2.2.2.4.2, and 2.2.2.4.3, respectively). The reactions of NMHC with HO$_2$, O, and O$_3$ play a minor role and will be neglected here, except for the reactions of alkenes with O$_3$. In addition, the further discussion will only focus on the oxidations of simple alkanes and alkenes. These pathways are representative for most of the NMHC.

The reaction with OH is the dominant loss process for alkanes within the troposphere, where the H atom is separated from the C-H bond ((103)) and forms an alkyl (R) radical. The subsequent reaction of the R radical with O$_2$ forms a RO$_2$ radical.

\[
RH + OH \rightarrow R + H_2O \quad (103)
\]

\[
R + O_2 \rightarrow RO_2 \quad (104)
\]

If R is CH$_3$ a third reaction partner is needed (reaction (23)). Ethane and propane can react in the following steps:

\[
RO_2 + NO \rightarrow NO_2 + RO \quad (87)
\]

\[
RO \rightarrow R' + R''CHO \quad (105)
\]

\[
RO + O_2 \rightarrow R'ROCO + HO_2 \quad (106)
\]

R' and R'' represent smaller alkyl radicals or organic groups. The aldehydes and ketones (R''CHO, R'R''CO) can be photolysed, as described for HCHO (see reactions (38) and (39)), or further oxidised. For instance the OH radical abstracts one H atom from the acetaldehyde and forms CH$_3$CO, which then reacts with O$_2$ to produce an acetyl peroxy radical (CH$_3$COO$_2$).

\[
CH_3CHO + OH \rightarrow CH_3CO + H_2O \quad (107)
\]

\[
CH_3CO + O_2 \rightarrow CH_3COO_2 \quad (108)
\]

The reaction of CH$_3$COO$_2$ with NO$_2$ is important, because it produces PAN.

\[
CH_3COO_2 + NO_2 \rightleftharpoons CH_3COO_2NO_2 \quad (109)
\]

The importance of PAN is based on the thermal equilibrium of reaction (109), which is shifted to the products side at lower temperatures. PAN represents a reservoir substance for NO$_x$. Under convective conditions air parcels can rise. This is in conjunction with lower temperatures in the free troposphere and the corresponding shift of the equilibrium of reaction (109) can favour the transport of NO$_x$ over large distances.
The subsidence of air parcels and the corresponding temperature increase moves the equilibrium back to the side of the educts. Resulting from this effect enhanced amounts of NO\(_x\) molecules can be transported into remote areas.

Another important pathway for CH\(_3\)COO\(_2\) is the reaction with NO (110). Through this reaction the resultant CH\(_3\)COO radical can be further fragmented (111):

\[
CH_3COO_2 + NO \rightarrow CH_3COO + NO_2 \quad (110)
\]

\[
CH_3COO \rightarrow CH_3 + CO_2 \quad (111)
\]

In the described reaction pathway larger alkyl radicals are fragmented to smaller alkyl radicals, until they are converted from CH\(_3\) into CO and CO\(_2\).

Ethene (C\(_2\)H\(_4\)) and propene (C\(_3\)H\(_6\)) react differently with OH. The alkenes form a complex with OH.

\[
OH + C_2H_4 \rightarrow HOC_2H_4 \quad (112)
\]

\[
OH + C_3H_6 \rightarrow HOC_3H_6 \quad (113)
\]

Both reactions show an intermediate state. In contrast to reaction (113), reaction (112) needs a stabilising collision partner (M). The two reactions show a negative temperature coefficient for the reaction rate constant, which is typical for an addition process.

In the case of reaction (113) a stabilised collision product was observed. The production of an OH-ethene adduct is exothermic (~ 134 kJmol\(^{-1}\)). However, the breaking of the C-H bond is endothermic (~ 30kJmol\(^{-1}\)), therefore the preferred reaction path is the decomposition back into the educts of reaction (112). The excess energy of the formed product from the propene with OH reaction (113) is comparable to reaction (112), but the abstraction of CH\(_3\) is energetically possible.

The alkene OH adducts predominantly react in analogy to the alkyl radicals. The subsequent oxygenation steps of the propene OH adduct are following:

\[
CH_3CHCH_2OH + O_2 \rightarrow CH_3CH(\overset{\cdot}{O})CH_2OH \quad (114)
\]

\[
CH_3CH(\overset{\cdot}{O})CH_2OH + NO \rightarrow CH_3CH(\overset{\cdot}{O})CH_2OH + NO_2 \quad (115)
\]

\[
CH_3CH(\overset{\cdot}{O})CH_2OH \rightarrow CH_3CHO + CH_2OH \quad (116)
\]

The reaction mechanism presented above is comparable to this formed by reactions (87), (105), and (106) for the R, RO\(_2\), and RO radicals. In the atmosphere, the CH\(_2\)OH reacts exclusively with O\(_2\), to form HCHO and HO\(_2\).

\[
CH_2OH + O_2 \rightarrow HCHO + HO_2 \quad (31)
\]
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The final products of the reaction of OH with propene, i.e. the aldehydes HCHO and CH$_3$CHO, are oxidised and photolysed as mentioned earlier. These reactions combined with the reaction of HO$_2$ with NO lead to a chain reaction. In general the oxidation of hydrocarbons is summarised as follows.

Cycle D:

\[
\begin{align*}
\text{OH + RH} & \rightarrow \text{H}_2\text{O} + \text{R} & (103) \\
\text{R} + \text{O}_2 + \text{M} & \rightarrow \text{RO}_2 + \text{M} & (104) \\
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 & (87) \\
\text{RO} + \text{O}_2 & \rightarrow \text{RCOR}^* + \text{HO}_2 & (106) \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 & (86) \\
2 \cdot \left( \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \left( ^3\text{P} \right) \right) & (84) \\
2 \cdot \left( \text{O} \left( ^3\text{P} \right) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \right) & (15)
\end{align*}
\]

net:

\[
\text{RH} + 4\text{O}_2 \rightarrow \text{RCOR}^* + 2\text{O}_3 + \text{H}_2\text{O}
\]

The chain carrier HO$_2$ and OH are converted into one another. The hydrocarbon RH will be oxidised under the consumption of four O$_2$ molecules to form two O$_3$ molecules. Finally, the net equation reveals the importance for the tropospheric O$_3$ production.

2.2.2.4.2 O$_3$ oxidation of NMHC

The mechanisms of the reactions of O$_3$ with alkenes are still not well understood. The initial step in the reaction is the addition of O$_3$ across the double bond to form what is known as a primary ozonide ((117)). The primary ozonide is not stable. One of the two peroxy O-O bonds and the C-C bond cleave simultaneously to give an aldehyde or ketone and a Criegee intermediate ((118)). The Criegee intermediate has excess energy, and can either be stabilized ((119)) or decomposed in a variety of ways.
Several studies in the literature [Horie et al., 1994, Gäb et al., 1995, Neeb et al., 1997, Wolff et al., 1997, Sauer et al., 1999] discuss the possible \( \text{H}_2\text{O}_2 \) production through the ozonolysis of alkenes and the subsequent reaction.

\[
\text{CH}_2 = \text{CHR} + \text{O}_3 \rightarrow \text{primary ozonide} \quad (117)
\]

\[
\text{primary ozonide} \rightarrow \text{CH}_2\text{OO}^+ + \text{RCHO} \quad (118)
\]

\[
\text{CH}_2\text{OO}^+ + \text{M} \rightarrow \text{CH}_2\text{OO} + \text{M} \quad (119)
\]

\[
\text{CH}_2\text{OO} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}_2 \quad (120)
\]

R represents the organic group and corresponds to H in the case of ethene. These reactions (117) to (120) are not the dominant pathways, but can contribute significantly to the total amount of \( \text{H}_2\text{O}_2 \).

In the recent literature there is some controversial discussion which questions whether production of \( \text{H}_2\text{O}_2 \) via this reaction path takes place at all [Geert Moortgat, personal communication, 2002]. Neeb et al. [1997] observed no significant production of \( \text{H}_2\text{O}_2 \), and the formation of HCHO linearly coupled to the consumption of alkenes. This indicates that HCHO is formed only as a primary product from the primary ozonide [Hatakeyama and Akimoto, 1994].

2.2.2.4.3 Cl oxidation of NMHC

In contrast to OH, Cl reacts only with the hydrocarbons and not with CO. The Cl with hydrocarbon reactions can either proceed by abstraction of a hydrogen atom from a C-H bond or proceed by addition to a for example double bond in the case of the hydrocarbon being an alkene. The most reaction rate coefficients of Cl with alkanes reactions ((121)) are up to 2 orders of magnitude faster than the corresponding OH. The reaction rate coefficients of the Cl and alkenes are approximately up to one order of magnitude faster than the corresponding OH.

\[
\text{RH} + \text{Cl} \rightarrow \text{HCl} + \text{R} \quad (121)
\]

Cl also reacts with aromatic hydrocarbons, but only at a significant rate with those having saturated chains from which the Cl can abstract a hydrogen or unsaturated side chains where it can add. For example, the reaction of Cl with benzene is slow \((k = 1.3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})\) [Shi and Bernhard, 1997]. On the other hand, the rate constants for the reactions with toluene, p-xylene, and p-cymene are high \((0.59x 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, 1.5x 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ and } 2.1x 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})\) [Shi and Bernhard, 1997, Finlayson-Pitts et al., 1999]. Hence reactions of aromatic
hydrocarbons with chlorine atoms will be primarily significant for those species having reactive groups attached to the ring.

Several atmospheric models have shown that larger amounts of Cl radicals are unlikely, because their presence would reduce the hydrocarbon concentrations to levels unrealistically low [Finlayson-Pitts, 1993b, Parrish et al., 1993, McKeen and Liu, 1993, Graedel and Keene, 1995, Wingenter et al., 1996].

Conversely, other scientists have estimated halogen concentrations in the order of $10^3$ to $10^6$ molecules cm$^{-3}$ on account of hydrocarbon measurements [Singh et al., 1996, Jobson et al., 1994, Wingenter et al., 1996].
2.3 Atmospheric chemistry modelling

The basis and the different approaches for the modelling of the atmosphere are presented within this section. The description of different chemical reaction types is followed by their numerical treatment. The main purpose is to show the general theoretical approach and to present in a transparent way the motivation to reduce the modelling efforts within this work towards a zero dimensional chemistry model.

2.3.1 Basics

All models which simulate atmospheric processes calculate, starting with the initial value, the time dependent variation of the concentrations of the individual gases $y_i$. The concentration for the time $T = t + dt$ results from the following mathematical expression:

$$\left[ y_i \right](T) = \left[ y_i \right](t) + \left( \frac{d\left[ y_i \right]}{dt} \right)_{\text{total}} dt.$$  \hfill (122)

The concentration of a certain species $y_i$ is indicated by the cornered brackets. The unit of concentration is [molec cm$^{-3}$]. This equation has to be solved for every species and for every considered location. The variations of the concentrations are calculated by an equation, which accounts for the variation caused by chemical processes as well as by transport, emission, and deposition (continuity equation):

$$\left( \frac{d\left[ y_i \right]}{dt} \right)_{\text{total}} = \left( \frac{d\left[ y_i \right]}{dt} \right)_{\text{transport}} + \left( \frac{d\left[ y_i \right]}{dt} \right)_{\text{chemistry/deposition}} + \left( \frac{d\left[ y_i \right]}{dt} \right)_{\text{emission}}$$  \hfill (123)

As this work focuses on the chemical evolution of the concentrations of different species, the transport and emission processes are not further described. The description of the atmospheric dynamics and their mathematical treatment can be found in Trenberth [1992] and Seinfeld and Pandis [1998].

The continuity equation for the variation of the concentration of species by chemical processes is:

$$\left( \frac{d\left[ y_i \right]}{dt} \right)_{\text{chemistry}} = P_i - L_i \left[ y_i \right]$$  \hfill (124)
where $P_i$ is the chemical production and $L_i$ is the chemical loss rate of the species $y_i$ at the considered location. The chemical loss processes are proportional to the concentration $[y_i]$ of that species. As deposition processes can be treated according to the k-theory like effective first order loss processes, there is no longer any separation between the chemical and the deposition mechanisms.

For the calculation of the chemical loss and production terms, the reaction rate coefficients of the involved reactions of each species $y_i$ are needed. They are determined within laboratory experiments and can be found in DeMoore et al. [1997], National Institute of Standards and Technology (NIST) Chemical Kinetics Database, Atkinson et al. [2000, International Union of Pure and Applied Chemistry (IUPAC)].

There are three different types of reactions:

a) bimolecular reactions: $A + B \xrightarrow{k_b} C + D$

b) termolecular reactions: $A + B + M \xrightarrow{k_t} C + D + M$

c) unimolecular reactions: $A(M) \xrightarrow{k_{uni}} C + D(M)$

In addition the two following reaction types are described explicitly, due to their particularity.

d) photolysis reactions: $A + hn \xrightarrow{j} C + D$

e) heterogeneous reactions: $A + B \xrightarrow{k_{het}} C + D$.

The reaction rate coefficients $k_b$, $k_t$, and $k_{uni}$ can be found in the literature mentioned above and models are typically in agreement with each other due to the relatively small uncertainty of the values the models use. Conversely, the calculation of the rate coefficients for the photolysis reactions and the heterogeneous reactions are more complicated and usually vary from model to model, because there is no conventional approach for neither of these processes.

The knowledge of the composition of the aerosols is essential for calculating the heterogeneous reaction rate coefficients $k_h$ in chemical models [Carslaw et al., 1995, Hanson et al., 1994]. As this work focuses on the gas phase chemistry, the heterogeneous chemistry is not considered. Nevertheless, the heterogeneous reactions involving the halogen production are discussed qualitatively, and assumptions are made for the resultant amounts of halogens in the gas phase. Different approaches for the
calculation of the composition of liquid aerosols are discussed in Carslaw et al. [1997]. A compendium of laboratory data and their implementation into chemical models is described in Ravishankara [1995, 1997], Sander and Crutzen [1996, 1999], Vogt et al. [1996, 1999].

The calculation of the reaction rate coefficient of the photodissociation, the photolysis frequency $j$, needs an even higher expenditure, because the rate of the photolysis reaction depends on the intensity of the light present in the atmosphere. The photolysis frequency depends predominantly on the solar zenith angle and consequently on the geographical position, the time of the day and on the time of the season. In addition the radiation itself is affected by the composition of the Earth’s atmosphere. The photolysis frequencies are necessary input parameters for atmospheric models and are typically independently calculated. Due to the very time consuming calculation of the photolysis frequencies, large models typically use simplified calculation schemes.

The calculation of the photolysis frequencies typically consumes more time than the equation (124) does. As a consequence, the photolysis reactions are only approximated within larger models.

The calculation of the photolysis frequencies is a main focus of this work. Therefore the validation and the limitations of the used model are extensively discussed in chapter 4.2.3.1.

### 2.3.2 Different model types

The present understanding of atmospheric processes has achieved a level at which it is possible to realistically simulate the behaviour of the atmosphere. The use of models and their validation with measurements gives the opportunity to identify deficits of the current knowledge of atmospheric mechanisms, and in combination with specific laboratory studies and atmospheric observations, to solve these deficits.

For the description of the Earth’s atmosphere several different types of models are used. Any particular type of model is selected according to the initial purpose. The limitation of the computing power restricts the complexity of a model.

The simplest models are the so called box models or 0-D-models. These models assume that the chemical reactions take place in an isolated area (box). Simple concepts are used for the parameterisation of the entrainment of other air masses into the box.
The main application of box models is to investigate the influence of specific reactions, reaction cycles [Crutzen et al., 1992, Danilin et al., 1996, Sander and Crutzen, 1996, Vogt et al., 1996, Dickerson et al., 1999], or different approximations on the results like the calculation of photolysis frequencies [Lary and Pyle, 1991, DeMajistre et al., 1995]. In the latter case the Box is fixed at a certain location, and the parameter pressure and the temperature are varied (Eulerian model). The importance of the individual reactions can be determined with different model runs. The combination of both applications is described in Finkbeiner et al. [1995].

The first extension of the box models leads to the 1-D-models. Typically, several boxes are piled up, and the atmosphere is simulated simultaneously in different altitudes. In addition, there is vertical exchange between the boxes. Typical applications are the investigation of the effect of different emission scenarios of chlorofluorocarbons (CFCs) on the amount of stratospheric $O_3$ [Brühl and Crutzen, 1988], or the comparison of vertical profiles of measurements with model results [Froidevaux et al., 1985, Allen and Delitsky, 1991, Wagner et al., 2002]. Based on their measurement geometry especially balloon soundings are frequently used for comparisons with 1-D-models [Chance et al., 1996, Renard et al., 1996]. The horizontal transport is commonly ignored in 1-D-models, because it is negligible on the small time intervals used in the simulations.

Beside this application there are 1-D-models adapted to the measurement geometry of certain measurement techniques. For example, the atmospheric zenith sky measurements determine the trace gas concentrations along the light path of the sunlight through the atmosphere (slant column). The interpretation of results requires the conversion of slant into vertical columns. Therefore, the boxes are arranged in order to fit the path of the sunlight [Solomon et al., 1987, Fish et al., 1995].

The 2-D-models are the next step in the development of atmospheric models. These models calculate individual boxes in two directions in space, typically the altitude and the latitude. The models average in the zonal direction, which means that they assume the variation in zonal direction is smaller than the variation in meridional and vertical direction. Since the 80’s several models of this type exist, and they are continuously improved [Jackman et al., 1988, WMO 1995].

Accounting for transport within the 2-D-models enables the investigation of other aspects, like for example the global ozone distribution of the past decades [Solomon et al., 1996] and the impact of aircraft emissions [Tie et al., 1994]. However,
the required computing time increases strongly compared with 1-D-models, proportionally to the number of boxes considered. In addition, the zonal averaging makes the comparison with observations difficult.

3-D models are designed to solve the latter problem. There are two different approaches:

- Uncoupled 3-D-models are models in which the dynamics are calculated or meteorological data are measured, before they are used as input variables for the chemical model. As a consequence, it is possible to simulate a specific region (or globally) for a limited time period and to validate the results with measurements. Two famous models of this type are SLIMCAT [Chipperfield et al., 1997] and REPROBUS [Lefèvre et al., 1994]. The forecast ability of these models is reliable only as long as the chemical change has no impact on the dynamics.

- Coupled 3-D-models are models in which a general circulation model is coupled with a chemistry model. As a consequence, while the confidence of forecasting longer time intervals is enhanced, the overall precision of the model is reduced. The latter is caused by the uncertainty of the general circulation model compared with uncoupled dynamic calculations involving measurements of meteorological parameters. The development of the coupled 3-D-models is not very advanced [Steil et al., 1998]. Especially the needed computing capacity exceeds the available computing capacity by far.

All models which account for the horizontal transport, have to simplify the chemical description of the atmosphere due to insufficient computing capacity. These partly rough approximations are typically made in the calculation of the photolysis frequencies, in the reaction rate coefficients for heterogeneous reactions, sometimes in the numerical solving of the chemical equations, and in certain reaction cycles.

The observed discrepancies between simulations and observations might therefore be caused by the approximations in the model and can hardly be a proof for missing reactions. As a consequence, the multi dimensional models are not appropriate for the detailed investigation of the chemistry of the atmosphere.
Exclusively the 0-D-models enable the implementation of all relevant chemical processes without rough approximations, and therefore the investigation of their impact on the composition of the atmosphere. The influence of transport processes on the results of the simulation can be minimised, when the simulations are constrained to the measurements of the long lived species. The different temporal scales of dynamic processes and lifetimes of several trace gases are shown in Figure 16.

Figure 16 indicates which trace gases have to be constrained to the measurements depending on the time of simulation and the possible influence of the different dynamical processes.

![Figure 16: Temporal scale of dynamical processes and of the lifetimes of several trace gases [P.S. Monks, Uni-Leicester]](image-url)
2.3.3 The structure of chemical models

As it is already described in chapter 2.3.1, the chemical evolution of the concentration of the species $y_i$ is expressed by the continuity equation

$$\frac{d[y_i]}{dt} = P_i - L_i[y_i]. \quad (124)$$

To calculate the evolution of the species $y_i$, the production and loss terms have to be known. There are five different reaction types, which is discussed in the following.

2.3.3.1 The reaction rate coefficients

2.3.3.1.1 Bimolecular reactions

Bimolecular reactions can be represented as:

$$A + B \longrightarrow C + D.$$ 

Bimolecular reactions are the most important ones within the Earth’s atmosphere. They are second order reactions, which means that their velocity is proportional to the product of two concentrations. The variation of the concentration of $A$, $B$, $C$, and $D$ results from the following expression:

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = - \frac{d[C]}{dt} = - \frac{d[D]}{dt} = -k_b[A][B] \quad (125)$$

where $k_b$ is the reaction rate coefficient for this reaction.

The value and the temperature and pressure dependence of the reaction rate coefficient is determined in laboratory studies. The temperature dependence of most of the bimolecular reactions can be described with the Arrhenius law:

$$k_b = A e^{-\frac{E_a}{RT}} \quad (126)$$

where $A$ is the Arrhenius factor, $E_a$ the activation energy, $R$ the gas constant, and $T$ the temperature. The unit of the of $k_b$ is $[\text{cm}^3\text{molec}^{-1}\text{s}^{-1}]$ resultant from equation (125). The values for $A$ and $E_a$ or $E_a/R$ for the most important atmospheric reactions are tabulated in DeMoore et al. [1997], National Institute of Standards and Technology (NIST) Chemical Kinetics Database [1998], Atkinson et al. [2000, International Union of Pure and Applied Chemistry (IUPAC)].
There are two different categories of bimolecular reactions: the direct and the indirect reactions.

**Direct bimolecular reactions**

The course of the direct bimolecular reaction can be explained by a collision process, which activates an excited state which falls apart into the final products.

\[
A + B \rightarrow (AB)^* \rightarrow C + D
\]

The Arrhenius factor depends on both the collision frequency and the geometry of the participating molecules. This is because a reaction can only occur when the molecules are orientated to each other in the right direction. The maximum value for the Arrhenius factor \((3 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})\) results from the collision theory under the assumption of spherical and solid particles at 300 K. The collision frequency is proportional to the Arrhenius factor with \(\sqrt{T}\), but this dependency is neglected within the Arrhenius law.

The temperature dependence of \(k_b\) is caused by the necessary overcome of the positiv activation energy \(E_a\), in order to achieve the intermediate state \((AB)^*\). The fraction of molecules with sufficient energy is given by the Maxwell distribution and therefore is proportional to \(e^{-\frac{E_a}{T}}\).

Direct bimolecular reactions are not pressure dependent. The Arrhenius law can well describe the temperature dependence of the reaction rate coefficients between 200 and 300 K [DeMoore et al., 1997].

**Indirect bimolecular reactions**

The indirect bimolecular reactions are characterised by their negative activation energy. This property cannot be explained by a simple theory. In the course of the reaction a relatively stable intermediate is formed

\[
A + B \rightleftharpoons [AB]^* \rightarrow C + D
\]

where \([AB]^*\) is stable, and can therefore exist for a longer period of time, than \((AB)^*\), which is unstable and cannot be determined experimentally.

The dependence of the reaction rate coefficients of indirect bimolecular reactions on the temperature and pressure can be much more complicated than for direct bimolecular reaction rate coefficients. If \([AB]^*\) reacts to form C and D or if it falls apart back into A and B, it will be a function of the energy of \([AB]^*\), which will therefore
strongly depend on the temperature and pressure (i.e. for example \([AB]^*\) is more stable at lower temperatures, thus tends to produce more C and D).

An example for an indirect bimolecular reaction, where the temperature dependence resultant from the laboratory studies fits with the Arrhenius law, is

\[
\text{ClO} + \text{NO} \longrightarrow \text{NO}_2 + \text{Cl}, \quad k_b = 6.4 \times 10^{-12} e^{\frac{290}{T}}
\]

where neither pressure nor complex temperature dependence was observed.

An example for an indirect bimolecular reaction with a complex temperature and pressure dependence is

\[
\text{HNO}_3 + \text{OH} \longrightarrow \text{H}_2\text{O} + \text{NO}_3, \quad k_b = k_0 + \frac{k_3[M]}{1 + \frac{k_3[M]}{k_2}},
\]

where \(k_0, k_2,\) and \(k_3\) are experimentally determined.

### 2.3.3.1.2 Termolecular reactions

Termolecular reactions are described by the following expression,

\[
A + B + M \longrightarrow C + M
\]

where \(M\) is a collision partner, typically \(\text{N}_2\) or \(\text{O}_2\) in the Earth’s atmosphere. The collision partner is needed to conserve the impulse, but also to energetically stabilise the intermediate. The variation in the concentration of the participating species can be determined by

\[
\frac{d[A]}{dt} = \frac{d[B]}{dt} = -\frac{d[C]}{dt} = -k_i [A][B]
\]

(127)

However, the calculation of the termolecular reaction rate coefficient \(k_i\) is not as simple as it is with the Arrhenius law, because the dependence on pressure and temperature is, due to the need of a collision partner, complex.

The termolecular reaction can be described by two sub steps:

1. activation: \(A + B \longrightarrow C^*\)
2a. stabilisation: \(C^* + M \longrightarrow C + M\)
2b. back reaction: \(C^* \longrightarrow A + B\).

First of all the intermediate \(C^*\) has to be formed (1.). Then the intermediate can either be stabilised (2a.), which means that the excess energy is transferred to the
collision partner M, or can react back to the initial products (2b.). Only if the excited state C\textsuperscript{*} is stabilised the reaction will take place.

The theory for describing termolecular reactions has been developed by Rice, Ramsberger, Kassel, and Marcus (RRKM) [Wayne, 1991a] and is based on the exact calculation of the different excited states of the molecules. This method excellently expresses the measured reaction rate coefficients and their pressure and temperature dependences. However this theory is not suitable for being implemented into a model. Therefore, an appropriate parameterisation of the reaction rate coefficient has been developed [Troe, 1983]. The equation for the reaction rate coefficient is as follows:

\[
k_i(M,T) = \frac{k_0(T)[M]}{1 + \left(\frac{k_0(T)[M]}{k_\infty(T)}\right)} \cdot F(M,k_0(T),k_\infty(T))
\] (128)

where \(k_0\) is the threshold for the reaction rate coefficient for low pressure:

\[
k_0 = \lim_{[M] \to 0} k_i(M,T).
\] (129)

In the low pressure range \(k_i\) is proportional with [M] and therefore with the pressure. \(k_\infty\) is the threshold of the reaction rate coefficient for high pressure:

\[
k_\infty = \lim_{[M] \to \infty} k_i(M,T).
\] (130)

For this conditions \(k_i\) is independent on the pressure. The function \(F(M, k_0(T), k_\infty(T))\) is called broadening factor. It describes the turnover between the two pressure regions. \(F\) can be analytically solved for atmospheric temperatures as follows:

\[
\log_{10} F \equiv \frac{\log_{10} F_C}{1 + \left(\frac{\log_{10} \left(k_0(T)[M]\right)}{k_\infty(T)\right)^2}
\] (131)

where the value for \(F_C\) has to be given. The equation includes a simplification, which under special circumstances can lead to significant discrepancies in comparison with the exact calculation (RRKM).

The temperature dependence is fitted to the measured data by the following relation:

\[
k_{0(\omega)}(T) = k_{0(\omega)} 300 \left(\frac{T}{300}\right)^{-\alpha(n)}
\] (132)
The exponent \( n \) is selected for \( k_0 \) and the exponent \( m \) is used for \( k_\infty \). The reaction rate coefficients \( k_t \) for the termolecular reaction can also analytically be calculated with \( k_0^{300} \), \( n \), \( k_\infty^{300} \), \( m \), and \( F_C \). In DeMoore et al. [1997] \( F_C \) has a constant value for all reactions, so that only four parameters are tabulated. The values for \( k_0^{300} \), \( n \), \( k_\infty^{300} \), \( m \), and \( F_C \) do either come from measurements or from model calculations with the RRKM theory.

All four respectively five parameters can be found in DeMoore et al. [1997], National Institute of Standards and Technology (NIST) Chemical Kinetics Database [1998], Atkinson et al. [2000, International Union of Pure and Applied Chemistry (IUPAC)]. An investigation of the simplifications made in the broadening function in equation (131) showed differences between 10 and 30\% for \( k_t \) at atmospheric pressures in comparison with measurements and exact model calculations [Donahue et al., 1997].

A very important termolecular reaction is the production of \( O_3 \) by the reaction of \( O(^3P) \) with \( O_2 \).

\[
O_2 + O(^3P) + M \rightarrow O_3 + M, \quad k_t = 6 \cdot 10^{-33} [M] \left( \frac{T}{300} \right)^{-2.3}
\]

Within the range of atmospheric pressures this reaction is linearly dependent on the pressure.

Another termolecular reaction of major importance in the Earth’s atmosphere is the reaction of \( NO_2 \) with OH.

\[
NO_2 + OH + M \rightarrow HNO_3 + M
\]

### 2.3.3.1.3 Unimolecular reactions

Unimolecular reactions, e.g. thermal decomposition reactions can be described by

\[
A (+M) \rightarrow C + D (+M).
\]

The variation of \([A]\) results from

\[
\frac{d[A]}{dt} = -k_{uni} [A]
\]

These reactions are pseudo first order, because the reaction rate coefficient \( k_{uni} \) is strongly dependent on temperature and pressure. The unit for \( k_{uni} \) is \([s^{-1}]\). Obviously the reaction is faster at higher temperatures and higher pressures, because the number of
collisions increases. In addition the many species are thermally unstable, thus a higher
temperature enhances their decomposition.

These reactions are the back reactions of the termolecular reactions, which
means they can be parameterised in the same way as used in Atkinson et al. [2000]. The
temperature dependence of $k_0$ and $k_\infty$ is parameterised with the Arrhenius equation.

In DeMore et al. [1997] the equilibrium constants $K_{eq}$ for the termolecular
reaction are given, where the reaction rate coefficients can be calculated from.

$$k_{uni} = \frac{k_i}{K_{eq}}$$  \hspace{1cm} (134)

An important thermal decomposition reaction is the breakdown of $N_2O_5$.

$$N_2O_5 + M \rightarrow NO_2 + NO_3, \quad K_{eq} = 2.7 \cdot 10^{-27} e^{\frac{11000}{T}}$$

This equilibrium constant was determined in several independent experiments
[DeMore et al., 1997].

The experimental errors of the reaction rate coefficients of the uni-, bi-, and
termolecular reactions are always above 20% [DeMore et al., 1997]. Especially the
determination of the temperature dependence is associated with larger errors.

### 2.3.3.1.4 Photolysis reactions

The photolysis reactions

$$A + h\nu \rightarrow C + D$$

are first order reactions, which means that the temporal variation can be
computed by

$$\frac{d[A]}{dt} = -j[A].$$  \hspace{1cm} (135)

$j$ is the photolysis frequency in units of $[s^{-1}]$. The reaction constant depends on
the light intensity as well as the molecule properties (absorption cross section and
quantum yield).
### 2.3.3.1.5 Heterogeneous reactions

Heterogeneous reactions take place at the liquid and solid particles (aerosols) in the atmosphere.

\[
A + B \xrightarrow{\text{het}} C + D
\]

Typically, these reactions are treated as first order reactions. Therefore the temporal variation can be expressed as

\[
\frac{d[A]}{dt} = -k_{\text{het}} [A]. \tag{136}
\]

The reaction rate constant can be calculated with

\[
k_{\text{het}} = \frac{\omega A \gamma}{4} \tag{137}
\]

where \(\omega\) is the thermal velocity, \(A\) the surface of the particle and \(\gamma\) the uptake coefficient [Ravishankara, 1997]. The uptake coefficient is the probability that the reaction takes place in the case of a collision between the molecule and the particle happens. The calculation of the available surface and the uptake coefficient have large uncertainties. The experimental determination of \(\gamma\) and the determination of the basis of the physicochemical parameters, as the Henry-Law’s-Constant to calculate \(\gamma\) in models, belong to the most extensive laboratory studies within this field. An detailed discussion of heterogeneous chemistry can be found in Ravishankara [1997].

### 2.3.3.2 Solving of the differential equations

For calculating the temporal evolution of the concentrations, the equation (124) has to be solved for each participating species \(y_i\). As a consequence a coupled non-linear system of \(n\) equation results, where \(n\) is the number of considered species.

A problem occurs while solving this system, because the reaction rate coefficients vary by several orders of magnitude. The concentrations of single gases therefore vary with different velocities, in particular the photolysis frequencies change additionally with the time of the day. This is called a system of stiff differential equations.

In general, a system of ordinary differential equations (ODE) with given initial values can easily be solved. It starts with

\[
\frac{dy_i(t)}{dt} = f_i(t, y_1, \ldots, y_n), \quad i = 1, \ldots, n. \tag{138}
\]
where the functions $f_i(t,y_1,...,y_n)$ are known. When the initial values $y_i(t_0)$ are known, it is possible to solve the system by changing the infinite $dy_i$’s and $dt$ into finite steps $\Delta y$ and $\Delta t$. One obtains $y(t=t_0+\Delta t)$ as the sum of $y(t_0)$ and $\Delta y_i(t_0) = f_i(t_0, y_1, ..., y_n) \Delta t$. This method with a suitable step size for $\Delta t$ leads in a good approximation to the exact solution of the differential equations, and the step size determines the accuracy.

To achieve an acceptable accuracy, the step size has to be smaller than the time in which the solution varies significantly, i.e. smaller than the time constants. This circumstance leads to problems within stiff differential equation systems as they appear in the atmospheric chemistry. Some reactions need small time steps for their fast reaction rate coefficients whereas smaller reaction rate coefficients need larger integration intervals. This can lead to numerical instabilities of the solution.

There are two different solution methods for ODE’s, the explicit and the implicit. The explicit solutions are described with the following formula:

$$y(t+\Delta t) = y(t) + \Delta y'(t).$$  \hspace{1cm} (139)

The new value $y(t+\Delta t)$ results from the derivation at the time $t$, therefore from $f_i(t, y_1, ..., y_n)$. The usage of explicit solution methods is inappropriate to solve stiff differential equations [Press et al., 1992].

Stiff differential equation systems can only be solved by implicit methods. The implicit method calculates the value for $y(t+\Delta t)$ not from the derivation at the time $t$, but at the time $t+\Delta t$:

$$y(t+\Delta t) = y(t) + \Delta y'(t+\Delta t).$$  \hspace{1cm} (140)

This method does not guarantee stability, but is much more reliable than the explicit method. The problem of the implicit method is that the derivation at the time $t+\Delta t$ is unknown, which means that the derivation has to be either calculated or approximated.

There are several different approaches for implicit solution methods to solve stiff differential equation systems [Press et al., 1992].

A frequently used implicit method for solving stiff differential equations is the Predictor-Corrector-method, where the derivation at the time $t+\Delta t$ is calculated with an iterative technique. An advantage of this method is that the time step $\Delta t$ is determined by the algorithm itself dependent on the needed accuracy.
The method given by Gear [1971] is based on this technique. The Gear’s method determines the derivation at the time \( t + \Delta t \) considering and extrapolating the earlier derivation with the help of the Backward Differential Formular (BDF) with fixed coefficients. This method has been used within the atmospheric chemistry since decades and has established itself as a reference for other methods used for solving chemical differential equations. The Gear’s method is used for example in FACSIMILE [AEA Technology, 1994] and in ASAD (A Self-contained Atmospheric chemistry coDe) [Carver et al., 1997]. The latter code is used in the present work for solving the reaction schemes in the developed model.
3 Experimental

This section gives an overview of all the techniques and analysis procedures for the measurement, determination and/or modelling of the species and parameters used for the interpretation of the present work. Some of the measurements were provided by other scientific groups involved in the corresponding experimental campaigns. The section is divided into the “INDOEX campaign” and for the “PRIME campaign”.

3.1 INDOEX campaign

The INDOEX campaign, an international research initiative, studied the chemistry of remote areas of the Indian Ocean and the influence of the outflow from the Indian subcontinent on these regions. This campaign took place during February, March, and April 1999.
Figure 17: The Indian Ocean Experiment (INDOEX) 1999 [http://www-indeoex.ucsd.edu/index.html].
Chapter 3: Experimental

3.1.1 RO$_2^*$ measurement technique

Peroxy radicals were measured continuously during the INDOEX campaign by using the chemical amplification technique (PERCA). This measurement technique is based on the conversion of peroxy and oxy radicals into an amplified, NO$_2$-modulated signal. The latter is detected by the chemiluminescence produced from the reaction of NO$_2$ with a Luminol solution [Hastie et al., 1991, Clemishaw et al., 1997, Burkert et al., 2001a]. The PERCA measures the sum of HO$_2$, OH, RO and RO$_2$ radicals, which to a good approximation can be considered to be equivalent to RO$_2^*$. The amplification of the signal, i.e. the chain length (CL) of the chain reactions, and the conversion factor for the individual organic radicals must be determined by adequate calibrations. The radical calibration source utilises the photolysis of H$_2$O in air at 185 nm [Schultz et al., 1995]. The PERCA and the calibration technique have been described in more detail elsewhere [Hastie et al, 1991, Volz-Thomas et al., 1998, Burkert et al., 2001b].

The response of the instrument is calibrated regularly by adding different dilutions of the NO$_2$ flow emitted from permeation tubes held at constant temperature. The PERCA used at the IUP-UB has been described more in detail elsewhere [Volz-Thomas et al., 1998, Stöbener, 1999, Burkert et al., 2001b, 2002a]. In this system, 3.3 ppmv NO and 9.9 % v/v CO are mixed with a flow of outside air in a glass reactor. This reactor comprises a 3 cm long nose of 4 mm internal diameter which expands into a cylinder of 2 cm diameter and 22 cm length. The air sampled is pumped through a homemade NO$_2$ luminol detector at a constant flow rate of 2 sLmin$^{-1}$. The chemiluminescence is produced from the reaction of NO$_2$ with a 5x10$^{-4}$ M luminol solution on a Whatman glass fibre filter paper. The number of photons produced via the chemiluminescence is measured by a photomultiplier tube. In order to assure that the sampled concentrations lie within the linear response regime of the NO$_2$ detector, the output of a NO$_2$ permeation tube is continuously added to the flow of air CO and NO, prior to the detector. This provides an offset NO$_2$ concentration, which is a convenient measure of the instrument response.

Data are acquired at 1 Hz using a Data Translation interface and Agilent Vee software which switches three way valves in the inlet system every 30 s. This yields an alternating signal comprising the radical amplification and the radical destruction modes, hereafter called signal and background modes respectively. Fifteen seconds of each mode are used to determine the average signal. Successive background modes are
averaged and subtracted from the signal mode. Finally, one minute averages of the radical signal are stored.

The whole system is mounted in a portable rack. Gas flow rates are controlled by MKS mass flow controllers. Both input and exhaust gas flows are purified using appropriate chemical converters: e.g. charcoal/iodine remove iron and nickel carboxyls from CO, FeSO$_4$ removes traces of NO$_2$ in NO, and activated charcoal with Pt/Al pellets at a temperature $T > 100 \, ^\circ\text{C}$ converts the CO in the exhaust to CO$_2$.

The chain length (CL) of the conversion reaction is determined with the aid of a calibration system based on the production of radicals from the UV photolysis of H$_2$O [Schultz et al., 1995].

The CL has recently been shown to be dependent on the relative humidity of the air sampled [Mihele and Hastie, 1998]. Therefore, the CL values obtained from a calibration under dry conditions were corrected according to the water dependency characterised in laboratory experiments for the IUP-UB set up. The reason for this dependency is still a subject under research [Mihele et al., 1999, Salisbury et al., 2001, Reichert et al., 2003].

During INDOEX, NO$_2$ and radical calibrations for the PERCA were performed twice a day and once a week respectively. The average CL, determined from all the radical calibrations performed in dry air during the measurement period, was 159 for the first leg, 136±13 for the second leg and 122±13 for the third leg. The steady decrease of the CL, observed during the whole campaign, is most probably caused by increasing contamination of the 20m long inlet system with sea salt, in spite of the regular cleaning of the reactor.

The temperature and the relative humidity of air entering the PERCA were assumed to be that provided by the data system of the ship. The detection limit is estimated to be 3-5 pptv RO$_2^*$ for 1-min values. The precision of peroxy radical calibrations is $\sim 15\%$, and a maximum uncertainty of $\pm 30\%$ is estimated for $1\sigma$ and 1 minute RO$_2^*$ values.

The inlet of the system was mounted on a mast located at the bow of the ship approximately 20 m above the sea level. The PERCA detector was inside an air-conditioned container on the deck.
3.1.2 CO measurement technique

CO was measured with a modified commercial nondispersive infrared gas filter correlation analyser (TEI model 48C, Franklin, MA) [Dickerson and Delany, 1988, Parsons and Dickerson, 1999] acquired at 1-min resolution.

3.1.3 O₃ measurement technique

O₃ was measured with a commercial UV photometer (TEI Model 49C, Franklin, MA), acquired at 1-min resolution. The complete dataset is reported by Stehr et al. [2002].

3.1.4 NO measurement technique

Nitrogen oxide was measured by a chemiluminescence detector built according to established protocols [e.g. Carroll et al., 1985]. The instrument is described in previous publications [Rhoads et al., 1997; Carsey, et al., 1997]. The detector was housed together with the PERCA, both inlets were fixed on the sampling tower. To avoid contamination by sea salt aerosols, the inlet line was capped by a 37-mm diameter 1-µm pore size Teflon filter (Gelman), replaced frequently during the cruise.

Airflow through the system was set to 1.2 L min⁻¹. The flow rate was calibrated periodically throughout the cruise with a bubble-flow meter (Sensidyne, Clearwater, Florida). A needle valve in the air line at the instrument rack further reduced the pressure and decreased gas travel time from the sampling point to the detector to less than 5 seconds. The NO was detected by measuring the chemiluminescent emission resulting from the reaction of NO with O₃ within a gold-coated stainless steel reaction chamber. Blank count rates were determined by reacting the gas stream with excess O₃ prior to entering the reaction chamber. The emitted photons were recorded by a 9658R photomultiplier tube (Thorn EMI) held at a potential of 1250 volts and contained in a cooled housing (Products For Research) maintained nominally at -40°C. Photon counting intervals of 10 seconds were recorded for the duration of the cycle. The first 2-3 minutes of each measure and calibrate count segments were ignored to allow the system to equilibrate. Each run was scanned for spikes or other anomalies due to other shipboard instrumentation. For the calibration a commercial calibration gas mixture (4.94 ppbv NO in N₂, Scott Specialty Gas) was injected into the inlet stream. Background count rates were higher than in previous experiments. The mixing ratios of
NO were obtained by subtracting the daytime (10 a.m. to 2 p.m. local time) average mixing ratios, from that obtained at night (10 p.m. to 2 a.m. local time).

### 3.1.5 NMHC measurement technique

Altogether 59 air samples, each having a volume of 9 L (STP), were collected in 2.5 L electropolished stainless steel canisters for the laboratory based analysis of NMHC. The air was sucked from the top of the bow tower (10 m height) via a stainless steel tube. Except during transport (~6 days) to the analytical laboratory (MPI-C, Mainz, Germany) the canisters were kept at −18°C and then equilibrated at ambient temperature for 12 h before gas chromatographic analysis. The condensable compounds (encompassing the NMHC) were first cryogenically concentrated at −170°C in a microtrap packed with porous silica beads, and thereafter were separated on a Al₂O₃/KCl porous layer open tubular (PLOT) column connected to a quadrupole mass spectrometer (HP 5973). Laboratory tests indicated detection limits (3σ variation of a blank sample) of 0.2-6.8 pptv for ethane, propane, butane, iso-butane, pentane and iso-pentane, and 14-26 pptv for acetylene. The precision for all species is 5-10 %. Comparisons with other laboratories showed agreements within ~20% for all species addressed here. For details, see Muehle et al. [2002].

### 3.1.6 $j$(NO$_2$) measurement technique

The frequency of photodissociation of NO$_2$ to NO and O($^3$P) was measured by determining the production of NO in a flow of NO$_2$ through a glass reactor of length 20 cm and volume 10 cm$^3$ (Kelley et al., 1995). In the standard manner, a black surface beneath the detector, yields the photolysis frequency of NO$_2$, $j$(NO$_2$):

$$j$(NO$_2$) = $\int I(2\pi)$,φ(NO$_2$, λ)$\sigma$(NO$_2$, λ)dλ.

Where I(2π) is the down-welling light flux at the surface, φ(NO$_2$, λ) the quantum yield for the dissociation of NO$_2$ and $\sigma$(NO$_2$, λ) the absorption cross section of NO$_2$.

2 l min$^{-1}$ of a mixture of NO$_2$ and air flowed constantly through the system. The NO and NO$_2$ mixing ratios were determined using a commercial detector (TEI model 42, Franklin, MA). The uncertainty with 95% confidence is estimated to be +/- 7% for values above 3x10$^{-3}$ s$^{-1}$ for 1 min average.
3.1.7 \( j(O^1D) \) measurement technique

The actinic UV flux was measured using a \( 2\pi \) sr filter radiometer with isotropic sensitivity (Meteorologie Consult GmbH, Germany), described by Junkermann et al. [1989] but having a filter combination optimised for cloudy conditions and high solar zenith angles. The \( O_3 \) column necessary to convert the recorded actinic UV flux into an \( O_3 \) photolysis frequency, \( j(O^1D) \), was measured many times each day aboard the RV Ronald H. Brown using a hand-held Microtops II sunphotometer (S/N 3685), having a 1-2% precision [Meywerk and Ramanathan, 2001]. The filter radiometer was compared with a spectroradiometer, described by Hofzumahaus et al. [1999] immediately after the INDOEX campaign. The \( j(O^1D) \) values ranged between 0 and \( 2.2 \times 10^{-5} \text{s}^{-1} \). The regression line exhibited a slope of 1.0; the linear correlation coefficient \( r^2 \) being 0.9989. The total uncertainty of the \( j(O^1D) \) data presented here is 15-20% for solar zenith angles (SZA) below 60°, increasing to 50% at SZA = 80° (including the current uncertainties in the \( O_3 \) absorption cross-section and \( O^1D \) quantum yield).

3.1.8 \( O_3 \) soundings

Sixty-one ozone and over sixty rawinsondes were launched twice a day, throughout the intensive field phase of INDOEX. Vertical profiles from 15ºS near Mauritius to 17ºN in the southeastern Arabian Sea were obtained [Herman Smit et al., personal communication, 1999]. The frequency of sampling increased when the ship approached the southwestern Bay of Bengal and during the ITCZ crossings.

The sondes used were balloon-borne ECC (Electrochemical Concentration Cell) ozone sondes (Model SPC-6A, Science Pump Corporation, New Jersey, USA) coupled to Väisälä radiosondes (Model RS80-15 H, Väisälä Finland). The error of the ECC ozone sensor is expected to be ± 1-2 ppbv below 5 km increasing to ± 5 ppbv at 10 km and ± 20 ppbv at 20 km altitude [Smit et al., 1994, 1998]. The response time of the ozone sensor is 25-30 seconds which corresponds to an ascent velocity of 5 m s\(^{-1}\) — this gives an altitude resolution of about 125-150 m.

The uncertainties in the temperature and pressure measurements below 20 km are ± 0.3ºC and ± 0.5 hPa respectively. The accuracy of the humidity sensor (HUMICAP-H) increases from ± 2% near the surface to ± 15-30% between 5-15 km altitude [Kley et al., 1997]. At low temperatures the response time of the sensor increases from about 200 sec. at -60ºC to 400 sec. at –70ºC [Antikainen and Paukkunen,
Above 15 km altitude the performance of the sensor is unreliable anymore [Kley et al., 1997].

### 3.1.9 Satellite data

The GOME instrument [Burrows et al., 1999] is a grating pseudo double monochromator covering the spectral range of 240 to 790 nm at a spectral resolution of 0.2 – 0.4 nm. GOME observes light scattered back from the atmosphere and reflected from the ground in near nadir viewing geometry. The GOME instrument was launched on board the European ERS-2 satellite in April 1995 and has been operational since July. The ERS-2 satellite is in a sun-synchronous polar orbit with an equator crossing time of 10:30 local time. The broad spectral coverage of GOME and the moderate spectral resolution allows the retrieval of a number of different trace gases that have structured absorptions in the UV and visible wavelength range. Under clear sky conditions, visible and near UV radiation reaches the surface, and provides GOME with a unique sensitivity towards tropospheric absorbers. In particular, GOME measurements have been used to study tropospheric SO$_2$ [Eisinger and Burrows, 1998], BrO [Wagner and Platt, 1998, Richter et al. 1998], HCHO [Wittrock et al., 2000, Thomas et al., 1998, Chance et al., 2001] and NO$_2$ [Leue et al., 2001, Velders et al., 2001].

In this study, tropospheric HCHO, O$_3$, and NO$_2$ columns are derived from GOME measurements. The absorption in a single earth-shine spectrum is derived using the Differential Optical Absorption Spectroscopy (DOAS) technique. The stratospheric NO$_2$ and O$_3$ contribution to this absorption is estimated using a measurement taken at the same latitude over the Pacific (180°-190° longitude), assuming the tropospheric amount of NO$_2$ and O$_3$ to be negligible and 22.5 DU, respectively, in this region. The assumption, however, of longitudinal homogeneity is reasonable only at low and middle latitudes [Richter et al., 2001]. The use of the Pacific region as a clean air reference is supported by results of both air-borne campaigns [Schultz et al., 1999, and references therein] and the GOME measurements themselves, indicated little or no influence of anthropogenic or lightning produced NO$_2$. The tropospheric O$_3$ is assumed to be constant, which is in fair agreement with measured O$_3$ soundings in this region [Thompson and Witte, 1999].

By subtracting the stratospheric column from the total column, a tropospheric slant column is derived that can be converted to a vertical tropospheric column using an
appropriate airmass factor (AMF). The AMF is defined as the ratio of the observed slant column to the vertical column and is calculated with a radiative transfer model SCIATRAN [Rozanov et al., 1997] using a model atmosphere. To minimise the bias introduced by clouds shielding the troposphere, only measurements with a cloud cover fraction below 0.1 are included in the analysis [Richter and Burrows, 2001]. The vertical tropospheric column of HCHO is derived from the slant column by using an appropriate tropospheric AMF. The stratospheric contribution is neglected.

The lightning produced NO$_2$ in the troposphere is measured as described above, but instead of using measurements with a cloud friction below 0.1, measurements concurrent with lightning activity are used. Lightning can be detected by NASA/NASDA-satellite project Lightning Imaging Sensor [Christian et al., 1999]. The air mass factor is corrected for influence of clouds, i.e. reflection at the top of cloud, multiple scattering in the clouds, single scattering below the cloud, and reflection at the surface [Hild et al., 2002].

3.1.10 Other supporting measurements

The meteorological parameters and backtrajectory analysis were taken from the INDOEX database and from the NOAA Pacific Marine Environmental Laboratory (PMEL) (for further information see http://www-indoex.ucsd.edu/index.html and http://saga.pmel.noaa.gov/indoex/index.html).

3.1.11 Modelling

The model, developed to simulate and investigate the chemical mechanism of the remote MBL, solves the time dependent set of differential equations using the atmospheric chemistry package ASAD (A Self-contained Atmospheric chemistry coDe) [Carver et al., 1997].

The chemical scheme accounts for 95 species and describes the chemistry of CH$_4$, CO, dimethylsulfide (DMS) and selected NMHC (C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, C$_3$H$_8$) [Burkert et al., 2001b, 2003a, 2003b, 2003c]. The oxidation of NMHC and DMS was assumed to produce HCHO or peroxy radicals in their reaction pathways, when the products of their reaction are unknown.

The chemistry of the MBL is described by 149 bimolecular, 30 termolecular and 21 photolysis reactions. Additionally the physical deposition of H$_2$O$_2$, CH$_3$OOH and O$_3$
at the sea surface is appropriately modelled. The reactions and reaction rate coefficients
have been collated from the IUPAC [Atkinson et al., 2000], JPL [DeMore et al., 1997]
and NIST (National Institute of Standards and Technology) Chemical Kinetics
Databases. The model does not take into account the dynamics, for example mixing,
advection or convection, and the remote marine boundary layer is considered to be an
effectively well mixed chemical reactor.

The photolysis frequencies were calculated by using PHOTOST an improved
version of the model PHOTOGT [Blindauer et al., 1996], which is based on the
radiative transfer model (RTM) SCIATRAN [Buchwitz, 2000]. To initialise the RTM,
in situ measurements of the aerosol optical depth (AOD) were used [Welton et al.,
2002]. The total ozone columns used in the model were measured by GOME [Burrows
et al., 1999 and references therein]. The aerosol composition used by the model was
adapted to measurements performed at Kashidoo Island [Lelieveld et al., 2001]. The
comparison of measured and calculated photolysis frequencies indicates that the
calculated photolysis frequencies are slightly overestimated for high AOD. The \(j(O(1D))\)
and \(j(NO_2)\) calculated photolysis frequencies at 30° SZA for AOD of 0 and 0.6 differ by
about 30% and 24% respectively [Burkert et al., 2003a]. In all simulations the
photolysis frequencies have been constrained to the measurements.
3.2 PRIME campaign

The PRIME campaign took place during July and August 1999 at the Silwood Park Atmospheric Research Station, near London (51°24′53″N, 0°38′48″W). The site offered the opportunity to measure on many days the plume from the city centre of London.

3.2.1 Overview of all measurement techniques

An overview of the measured trace gases together with a short description of the technique, calibration method, detection limit, and the time resolution is shown in Table 3.

<table>
<thead>
<tr>
<th>Species</th>
<th>Technique</th>
<th>Calibration method</th>
<th>Detection limit</th>
<th>Time resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>GFC</td>
<td>CO cylinder</td>
<td>20 ppbv</td>
<td>1 min</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>CL</td>
<td>NO + NO₂ cylinders</td>
<td>25 pptv</td>
<td>1 min</td>
</tr>
<tr>
<td>RO₂⁺</td>
<td>PERCA</td>
<td>NO₂ permeation tubes</td>
<td>5-10 pptv</td>
<td>1 min</td>
</tr>
<tr>
<td>PAN</td>
<td>GC</td>
<td>CH₃COCH₃ + hν + NO</td>
<td>100 pptv</td>
<td>10 min</td>
</tr>
<tr>
<td>H₂O₂,</td>
<td>HPLC</td>
<td>H₂O₂ cylinder</td>
<td>20 pptv</td>
<td>25 min</td>
</tr>
<tr>
<td>ROOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HO₂</td>
<td>FAGE</td>
<td>H₂O photolysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>FAGE</td>
<td>H₂O photolysis</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Measurements performed by IUP-UB and Uni-Leeds during the PRIME campaign. GFC: Gas filter correlation, PERCA: chemical amplification, CL: chemiluminescence, GC: gas chromatography, HPLC: high performance liquid chromatography.

3.2.2 RO₂⁺ measurement technique

The PERCA technique has already been described in detail in 3.1.1. Both NO₂ and RO₂⁺ calibrations were made regularly during the PRIME experiment. The CL averaged during the period of the campaign had a value of 165 for dry conditions. The detection limit is ~10 pptv for wet conditions (i.e. r.h. > 80%) for 10 min average and
decreases with decreasing relative humidity reaching levels of ~1-2 pptv for dry conditions. The 1 \( \sigma \) relative error is ~10% for 10 min averaged values.

### 3.2.3 OH and HO\(_2\) measurement techniques

HO\(_2\) was measured by the University of Leeds using the FAGE (Fluorescence Assay with Gas Expansion/Laser-Induced Fluorescence) technique for direct OH measurement. The HO\(_2\) measurement is accomplished by in situ conversion of HO\(_2\) to OH adding NO to the sample air stream [for details see Abram et al., 2000].

### 3.2.4 CO measurement technique

The Gas Filter Correlation (CFC) CO ambient analyser (Thermo Environmental Instruments Inc. Model 48) was used for the measurement of CO. The GFC spectroscopy is based upon comparison of the detailed structure of the infrared absorption spectrum of the measured gas to that of other gases also present in the sample being analysed. In the case of CO the technique is implemented by using a high concentration sample of CO as a filter for the infrared radiation transmitted through the analyser. CO and N\(_2\) are alternated producing a modulated signal with an amplitude related to the concentration of the CO in the sample cell.

Variations in temperature cause a drifting of the base line which is corrected by programming a zero measurement the first ten minutes of every hour. A five point calibration of the instrument was performed directly before the campaign.

### 3.2.5 NO and NO\(_2\) measurement techniques

The chemiluminiscence analyser MLU 200 AU was used for the monitoring of NO and NO\(_2\). The instrument measures the light intensity of the chemiluminiscence gas phase reaction of NO and O\(_3\). This reaction results in electronically excited NO\(_2\) molecules which release their excess energy by emitting a photon. The light intensity produced is directly proportional to the NO concentration present. A molybdenum converter, heated at 315°C, is used to reduce any NO\(_x\) present to NO. NO\(_2\) is obtained by subtraction of both values. The instrument has a detection limit of ~25 pptv NO for 1 min resolution and a relative error for the 1 \( \sigma \) confidence interval of 5% for 1 min averaged values.
The instrument was calibrated before and during the campaign. Both calibrations agreed within the experimental error.

### 3.2.6 PAN measurement technique

The PAN instrument (Meterologie Consult GmbH) consists of a gas chromatograph and a calibration unit. The measurement is based on the gas chromatographic separation of trace gases in the air sample followed by determination of PAN using an electron capture detector (ECD). Substances with high electronic affinity cause a decrease in the electronic density at the detector, which is compensated by a variation in the pulse rate at the electrodes of the detector. This variation is proportional to the amount of the substance in the sample. A sample is analysed every ten minutes and the system is calibrated regularly.

The calibration is based on the photolysis of acetone and the reaction of the formed peroxy acetyl radicals with NO to form PAN.

The detection limit is ~100 pptv and the 1 σ rel. error is ~10% for 10 min resolution.

### 3.2.7 H$_2$O$_2$ and CH$_3$OOH measurement techniques

This analytical technique uses high performance liquid chromatography (HPLC) with post column derivatization to separate and derivatize H$_2$O$_2$ and ROOH in any given sample. The peroxidase enzyme fluorescence technique is based on a method of Lazrus et al. [1986]. HPLC separation is achieved using an Merck LiChrospher C-18 reverse phase column with a mobile phase comprised of 10$^{-3}$ M sulphuric acid and 10$^{-4}$ M ethylenediamine tetraacetic acid solution supplied at a flow rate of 0.6 ml min$^{-1}$.

Samples are manually injected onto a 100 µl sample loop and flushed by mobile phase to the separating column. After separation hydroperoxides are derivatised to the stable dimer of p-hydroxyphenylacetic acid by addition of a reagent via a mixing tee. The reagent consists of 26mM p-hydroxyphenylacetic acid with 10$^5$ units l$^{-1}$ of horseradish peroxidase in 0.5 M potassium hydrogen phthalate buffer at pH 5.8. After reagent addition, adequate contact time is given for the rapid reaction of hydroperoxides with the derivatization reagent. The pH of the solution is raised to between 10 and 11 to convert the dimer into its fluorescent anionic form using a membrane reactor constructed of Nafion tubing immersed in 30% ammonium hydroxide solution.
Dimer quantification is achieved by fluorescence detection using a fluorescence detector with excitation and emission wavelengths of 310 nm and 405 nm respectively. Calibration of the HPLC is performed twice daily with fresh standards made by serial dilution of a 30% hydrogen peroxide solution in the range of $10^{-7}$ to $10^{-8}$, the concentration of which is determined by titration against potassium permanganate previously standardised with sodium oxalate.

The detection limit is ~20 pptv for 25 min resolution and the rel. error for 1 $\sigma$ confidence interval is ~15%.

### 3.2.8 Other supporting measurements

In addition to the measurements made by the IUP-UB and Uni-Leeds, many other relevant trace gases including O$_3$, HONO, CH$_3$O, carbonyls, H$_2$O, NMHCs, SO$_2$, aerosols, and photolysis rates ($j$(NO$_2$) and $j$(O($^1$D))) were measured along with standard meteorological parameters. Back trajectories were used for the air mass characterization [British Atmospheric Data Centre – Trajectory service, http://www.badc.rl.ac.uk/].

### 3.2.9 Modelling

A zero dimensional model was used to simulate the observed trace gas diurnal evolutions. The atmospheric chemistry package ASAD (A Self-contained Atmospheric chemistry coDe) is used for solving the time-dependent chemical reactions [Carver et al., 1997]. It consists of 138 species describing CH$_4$, CO and a minor set of NMHC oxidations, 243 bimolecular, 32 termolecular and 36 photolysis reactions, and includes the deposition of H$_2$O$_2$, CH$_3$OOH and O$_3$ [Burkert et al., 2001b, 2003a]. The reactions have been compiled from the NIST (National Institute of Standards and Technology) Chemical Kinetics Database. It is assumed that the partly unknown pathways of NMHC and DMS oxidations lead to HCHO or peroxy radicals. The heterogeneous reactions of NO$_3$ are not considered in the model.

The photolysis rates are simulated if not measured, using the model PHOTOST, an improved version of the model PHOTOGT, already described 3.1.11. The input data used in PHOTOST are from GOME (Global Ozone Monitoring Experiment) on board the satellite ERS2 [Burrows et al., 1999 and references therein] and aerosol optical depth values calculated from the $j$(O($^1$D)) measurements [Univ. Leeds, personal communication, 2002].
The model does not consider any dynamical processes. It has been successfully employed for the simulation of the diurnal evolution of trace gases measured over the Indian Ocean [Burkert et al., 2003a]. The mixing ratios of CH$_4$, NMHC, NO, NO$_2$, and CO have been constraint to the measurements on a 10 min base.
4 INDOEX campaign

The chapter that follows focuses on the analysis of the measurements performed during February, March, and April 1999 as a part of the Indian Ocean Experiment (INDOEX). The measurements were carried out on board the research vessel RV Ronald H. Brown above the Indian Ocean. The chapter is divided into two main subsections – “Trace gas and radical behaviour” and “Photochemistry and radiative effects of aerosols”.

4.1 Definition of air masses

Making use of the 6 days back-trajectories and the measurements of chemical and aerosol composition, four different types of dynamical regimes could be defined during the campaign [Ball et al., 2003]:

- Southern Hemisphere maritime Equatorial (SHmE), characterised as having a long transport over relatively pristine regions
- Northern Hemisphere maritime Equatorial (NHmE), characterised as having passed over relatively unpolluted regions
- Northern Hemisphere continental Tropical (NHcT), the air flow passing over India
- Northern Hemisphere continental extratropical (NHcX), the air flows passing over the Arabian Peninsula.

The cruise tracks and the daily position are presented in Figure 18. The prevailing airflow patterns during the three legs of INDOEX are shown in Figure 19. These overall patterns of air movement represent the average situation but there is significant local, spatial, and temporal variability.
Figure 18: INDOEX cruise tracks for leg 1-3, numbers along the track indicate day of the year (DOY).
Figure 19: Cruise track of the RV Ronald H. Brown during the 1999 INDOEX campaign and the cluster trajectories (950 hPa) showing the origin of the air masses encountered during the different segments of the cruise. The flow regimes are labelled SHmE, Southern Hemisphere marine equatorial; NHmE, Northern Hemisphere marine equatorial; NHcT, Northern Hemisphere continental tropical (subdivided in the sub-regimes Bengal and West); and NHcX, Northern Hemisphere continental extra-tropical.
4.2 Trace gas and radical behaviour

4.2.1 Introduction

The accurate measurement of trace gases over the ocean provides a particularly useful approach to assess the accuracy of atmospheric chemical models, because the simple dynamics and the lack of anthropogenic emissions, reduce the number of physico-chemical processes required to describe and interpret the results. This study describes trace gas and free radical measurements made in the remote marine boundary layer (MBL), during INDOEX an international research initiative, proposed to study chemistry of remote regions of the Indian Ocean and the influence of outflow from the Indian subcontinent on these regions [see Crutzen and Ramanathan, 2001, Ramanathan et al., 2001, Lelieveld et al., 2001, Ball et al., 2003, http://www-indoex.ucsd.edu].

One result of the Pre-INDOEX studies was the clear observation of strong diurnal cycling of O$_3$ having a minimum during the day [Rhoads et al., 1997]. Similar but generally weaker cycling has been occasionally observed in the most remote regions of the Atlantic ocean from the German research vessels Polarstern and Meteor in a series of cruises from 1987 to 1996 [Burkert et al., 2001b]. In addition to the loss of O$_3$ by the reaction with HO$_2$, evidence for a significant role of reactive halogens in the chemistry of the pristine MBL was inferred from an analysis of the Pre-INDOEX observations [Dickerson et al., 1999].

This study describes the measurements of RO$_2^*$, NO, NMHC, j(NO$_2$), j(O(1D)) and O$_3$ made from the National Oceanic and Atmospheric Administration (NOAA) research vessel RV Ronald H. Brown in the MBL. These observations continued those made within AEROSOL campaign, which made measurements from Norfolk Virginia via the North and South Atlantic into the Indian Ocean [Andrés-Hernández et al., 2001].

The cruise track of the RV Ronald H. Brown during INDOEX was similar to the track of the Pre-INDOEX cruise, which took place during the fall of 1995 [Rhoads et al., 1997]. One overarching goal of the AEROSOL and INDOEX campaign is to improve our knowledge of the fast photochemistry of the MBL. Specific objectives of this study are to assess the impact of aerosols on photolysis rates, the role of continental emissions on pollution levels in the remote marine atmosphere, and the link between levels of O$_3$ and RO$_2^*$. To achieve this objective the measured concentrations and
diurnal variation of $\text{RO}_2^*$ and HCHO [Wagner et al., 2001], predicted by a zero dimensional chemical model of the MBL have been compared with those measured to assess the possible role of multiphase and halogen chemistry in the budget of this species. The different behaviour of the observed amounts of $\text{RO}_2^*$ above the Atlantic and the Indian Ocean is also discussed in this study.

The following scientific issues and questions are raised and discussed in this paper: How do aerosols influence the photolysis frequency at ground level? Are the current parameterisations for the radiative properties suitable and appropriate? Are the measured amounts of $\text{RO}_2^*$ in agreement with that predicted by box model simulations? Are the observations of $\text{RO}_2^*$ and HCHO consistent and do they reflect the close chemical linkage between these constituents? Is the difference between HCHO measurements and model results observed during INDOEX different to the observations above the Atlantic Ocean [Weller et al., 2000]? Does the presence of $1 \times 10^4$-$1 \times 10^5$ molec cm$^{-3}$ amounts of reactive halogens provide a reasonable and plausible explanation of the unexpected behaviour of $\text{RO}_2^*$ and HCHO? What are the potential sources of reactive chlorine and bromine in the remote MBL? Do geographical or regional effects help to explain the difference between model results and measurements?

### 4.2.2 Results

#### 4.2.2.1 Characteristics of the different air masses observed

The four different air masses exhibited the following characteristics:

**SHmE (observed during DOY 54-58, 78.25-79.5)**

The SHmE regime showed the lowest mixing ratios for all trace species and in this sense was the least polluted air encountered. The maximum $\text{RO}_2^*$ mixing ratio during DOY 54 – 58 decreased with decreasing latitude from 35 to 25 pptv. The $\text{O}_3$ mixing ratio revealed the same behaviour, decreasing from 15 to 8 ppbv. The loss of $\text{O}_3$ per latitude decreased with decreasing latitude. The mean CO mixing ratio was 56 ppbv, the daytime average NO mixing ratio was below the detection limit of around 3 pptv. The NMHC mixing ratios were the lowest observed during the whole campaign. The mean values were: ethane 194 pptv, propane 7 pptv, and acetylene 21 pptv [Mühle et al., 2002]. The vertical profiles of $\text{O}_3$ mixing ratio showed a weak positive gradient with
increasing altitude up to 12 km between 12°S and the ITCZ, where the O$_3$ reached levels about 40 ppbv [Hermann Smit, personal communication, 2001].

**NHmE (observed during DOY 76-78.25, 79.5-81)**

In the NHmE regime the CO and O$_3$ mixing ratios were around 90 ppbv and approximately 10 ppbv, respectively. The maximum RO$_2^*$ mixing ratio varied between 55 – 60 pptv. The back-trajectories indicate a long travel time of the air parcel along the west coast of India. The NO mixing ratio was below the detection limit. Most of the NMHC doubled their mean mixing ratios compared to the SHmE air mass: ethane 332 pptv, propane 10 pptv, and acetylene 44 pptv. The vertical profiles of O$_3$ in this regime indicate an even weaker positive gradient in altitude compared to the SHmE regime, reaching levels of about 30 ppbv at 12 km.

**NHcT (observed during DOY 63-66, 74-76, 85-89)**

The NHcT regime was characterised by the highest observed maximum mixing ratios in RO$_2^*$ and CO during the whole campaign. Maximum levels of up to 90 pptv RO$_2^*$ and 200 ppbv CO were observed. NO measurements were higher than in the SHmE, but still close to the detection limit, around 6 pptv. The O$_3$ mixing ratios showed strong diurnal variations, with O$_3$ losses during the day being as large as 50%. The latitudinal gradient in O$_3$ was $\sim$ 1.25 ppbv/°latitude heading North. The NMHC main mixing ratios increased for ethane up to 403 pptv, propane to 20 pptv, and acetylene to 133 pptv. The vertical O$_3$ profiles revealed an enriched layer between 1 and 3 km having mixing ratios larger than 70 ppbv. The upper level O$_3$ values were different depending on the periods of observation. Back-trajectory analysis indicated that the air masses originated over India and the Bay of Bengal. The NHcT regime also appears to contain high concentrations of ash, soot, and other organic matter [Dickerson et al., 2002, Neusüß et al., 2002, Quinn, et al., 2002]. In addition the regime is heavily contaminated by fossil fuel combustion (indicated by sulphate), biomass burning (indicated by nss-potassium), and wind-blown mineral dust (indicated by ash and nss-calcium) [Ball et al., 2003, Quinn et al., 2002, Stehr et al., 2002]. The black carbon from India is currently considered to result mainly from internal combustion engines, biomass burning, and small-scale coal combustion. However, bottom-up estimates of black carbon emissions from India yield much smaller values than in situ observations do. This suggests an additional source not yet considered or unusually high emissions
factors [Dickerson et al., 2002]. Therefore a large uncertainty in the sources and/or emissions remains.

**NHcX (observed during DOY 66-74):**

The NHcX regime was characterised by the highest observed concentration of O$_3$ and NMHC at the most northerly point of the whole campaign. O$_3$ mixing ratios reached levels up to 53 ppbv and the NMHC averaged mixing ratios were: ethane 927 pptv, propane 133 pptv, and acetylene 169.3 pptv. The latitudinal gradient in O$_3$ remained ~ 1.25 ppbv/°latitude heading North. RO$_2^*$ and CO varied weakly around 55 pptv and 122 ppbv respectively. NO mixing ratios reached their highest values of the campaign being approximately 9 pptv. The vertical profile in O$_3$ showed the same behaviour as in the NHcT regime with an O$_3$ enriched layer above the MBL. The back-trajectories indicate that the air masses originated over the Arabian Peninsula.

### 4.2.2.2 Measurements trace constituents and parameters

#### 4.2.2.2.1 RO$_2^*$, O$_3$, and CO measurements

RO$_2^*$, O$_3$, and CO were continuously measured from DOY 54 to DOY 89. The observed RO$_2^*$, O$_3$, and CO diurnal cycles for the three legs are presented in Figure 20. The RO$_2^*$ mixing ratios showed the typical diurnal variation with the maximum occurring between midday and early afternoon. The RO$_2^*$ daytime maximum values varied from 25 to 90 pptv. CO concentrations did not show any significant diurnal variation, they only changed with different air masses. The CO values varied in the NH between 100 and 200 ppbv and in the SH between 40 and 70 ppbv.
Figure 20: Plots of the individual diurnal variation of $\text{RO}_2^*$, $\text{O}_3$, and CO observed on legs 1 to 3 of INDOEX. The classification of the air masses encountered are written above, the days and vertical lines separate the different types of air masses.
The \( \text{O}_3 \) mixing ratio typically decreases during daytime with a minimum close to sunset and a recovery during the night. In contrast to this behaviour the \( \text{O}_3 \) in leg 1 does not show any recovery at night and each day the average \( \text{O}_3 \) mixing ratio is smaller. This implies that the net photochemical losses during the day are equal to the latitudinal variation of \( \text{O}_3 \). The maximum values of \( \text{O}_3 \) varied in the SH between 8 and 15 ppbv and in the NH between 10 and 55 ppbv.

### 4.2.2.2 NO measurements

The NO data collection for INDOEX began on DOY 53. The average mixing ratio of NO in the SHmE air mass was 3 pptv, being comparable to the 4.8 pptv reported for the SHmE regime [Rhoads et al., 1997]. The average mixing ratio for NO within NHcT was 6 pptv, compared to 4.7 pptv found in the earlier cruise.

A summary of the measurements of NO associated with the different air mass type is given in Table 4.

<table>
<thead>
<tr>
<th>airmass design.</th>
<th>NO mixing ratio mean [pptv]</th>
<th>stddev.</th>
<th>Number of measurements (24 hour avg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHmE</td>
<td>3</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>NHcT</td>
<td>6</td>
<td>11</td>
<td>7</td>
</tr>
<tr>
<td>NHcX</td>
<td>9</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>NHmE</td>
<td>below detection limit</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 4: Averaged NO mixing ratios observed in four different air masses. Mixing ratios were computed as day-night differences.

The largest mixing ratios of NO were found within the NHcX air mass, where input from the Indian continental regions is expected to be low and the travel time over the ocean relatively long compared with that for the other air mass types, being about 3-5 days. Therefore, the NO was most likely transported in the upper layers of the troposphere, where the lifetime of NO is much longer compared to the MBL.

### 4.2.2.3 \( j(\text{O}(^1\text{D})) \) and \( j(\text{NO}_2) \) photolysis frequency measurements

In Figure 4, the measured \( j(\text{O}(^1\text{D})) \) and \( j(\text{NO}_2) \) photolysis frequencies for leg 2 of INDOEX and two selected days in the NH and SH, respectively, are shown. The variation in the maximum \( j(\text{O}(^1\text{D})) \) values indicates the large influence of the aerosols on the photolysis frequencies. The reduction is about 40\% for \( j(\text{O}(^1\text{D})) \) and about 22\% for \( j(\text{NO}_2) \).
Figure 21: a) Measured $j(O(^1D))$ photolysis rates for leg 2 (DOY 63 – 80) during INDOEX. b) Diurnal variation in the photolysis rate coefficient for NO$_2$; only cloud-free data are shown. Filled squares represent data from the clean, marine atmosphere on DOY 57 at 4°S with an AOD of about 0.07 at 500 nm. Open squares represent data from a polluted atmosphere over the northern Indian Ocean on DOY 65 at 6°N with an AOD of 0.4 at 500 nm.
Taking into account that more than half of the light driving the photolysis of $O_3$ to $O(^1D)$ is scattered “skylight” rather than direct sunlight, the sometimes observed small cumulus clouds have little impact and the assumption of clear sky conditions for the model used later on is therefore reasonable.

4.2.2.2.4 NMHC measurements

The NMHC measurements have been separated into the amounts of smaller (C<5) and larger (C>4) alkanes and are presented in Figure 22. Some of the data have already been presented by Mühle et al. [2002]. The highest amount of all alkane was observed in the NHcX regime, moderate levels being present in the NHcT regime and the lowest values were encountered in the NHmE: the latter being around half of that in the NHcT regime. The transition between NHcT and NHmE was gradual, and not as sharp as the transition between other air masses. Air masses, influenced by the Arabian Peninsula, contain the highest amounts of NMHC: the daily peak being up to twice as high as the average concentration.
Figure 22: NMHC, i.e. alkane and acetylene measurements in the NH during INDOEX (DOY 64 – 78) a) the lighter alkanes and acetylene, b) the heavier alkanes measured.
The observed decrease in the measured concentrations of the NMHC on DOY 66, 67, 72, and 73 cannot be explained by chemical destruction but rather by transport effects. The 800 mbar back trajectories, which originated over India, indicate an increasing downward mixing of NHcT air masses into the NHcX air masses in the MBL.

4.2.3 Discussion and Interpretation

In this section the measurements of trace constituents and parameters are analysed. Initially the photolysis frequencies, which were determined by calculation in the model, are compared with the ground based measurements. The role of aerosol on the photolytic radiation in the MBL is then discussed. Accurate knowledge of the photolysis frequencies is required as input for the chemistry of the box model.

4.2.3.1 Simulation of photolysis frequencies

Photolysis frequencies for the photolytic active trace gases were calculated in this study using PHOTOST, an improved version of the model PHOTOGT [Blindauer et al., 1996], which has been upgraded to use the radiative transfer model (RTM) SCIATRAN [Buchwitz, 2000] in place of its predecessor GOMETRAN [Rozanov et al., 1998]. To initialise the RTM, the in situ measurements of the aerosol optical depth (AOD) made during INDOEX were used [Welton et al., 2002]. These agreed with the observed sun photometer measurements [Meywerk and Ramanathan, 1999, Welton et al., 2002]. The photolytic radiation, encountered in the MBL during the INDOEX campaign, was determined in the model taking explicitly into account the following:

- Rayleigh single and multiple scattering by air molecules,
- O₃ absorption of ultraviolet radiation, the values of total O₃ column being those measured by GOME on board the ERS-2 satellite [Burrows et al., 1999 and references therein], all other trace gases were taken from a climatology database [Brühl and Crutzen, 1993].
- the effective surface spectral reflection at the ocean surface, albedo (α=0.05).

The underestimation of the actinic flux on account of neglecting the SZA dependence of the albedo is below 1% (SZA = 60°), 2.5% (SZA = 70°), 6% (SZA = 80°), and 8% (SZA = 90°) [Cox and Munk, 1954, Jin et al., 2002]
single and multiple scattering and absorption by aerosol, the aerosol parameters being defined in the model such that the aerosol composition and the aerosol optical depth (AOD) were compatible with the in situ and sun photometer measurements.

During INDOEX the aerosol composition of the MBL was continuously measured at the island station of Kaashidoo [Lelieveld et al., 2001]. The average of the entire dataset is shown in Table 5 a) and is used to describe the aerosol composition in the model. The atmosphere above the MBL contains only the Kaashidoo compositions, whereas the MBL contains a mixture between the a) Kaashidoo aerosol composion and b) sea salt aerosol composition, as described in Table 5 c).
a) non sea salt composition (nss)

<table>
<thead>
<tr>
<th>Type</th>
<th>Dry mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>31</td>
</tr>
<tr>
<td>Organics</td>
<td>25</td>
</tr>
<tr>
<td>Black carbon</td>
<td>15</td>
</tr>
<tr>
<td>Mineral dust</td>
<td>11</td>
</tr>
<tr>
<td>Ammonia</td>
<td>9</td>
</tr>
<tr>
<td>Fly ash</td>
<td>6</td>
</tr>
<tr>
<td>Minor components</td>
<td>3</td>
</tr>
</tbody>
</table>

b) sea salt composition (ss)

<table>
<thead>
<tr>
<th>Type</th>
<th>Dry mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water soluble</td>
<td>7.1</td>
</tr>
<tr>
<td>Sea salt (acc. mode)</td>
<td>90.8</td>
</tr>
<tr>
<td>Sea salt (coarse mode)</td>
<td>2.1</td>
</tr>
</tbody>
</table>

c) mixing in the model

<table>
<thead>
<tr>
<th>DOY</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>55-57; 78</td>
<td>87 % ss; 13 % nss</td>
</tr>
<tr>
<td>58-60; 63-67; 85-88</td>
<td>18 % ss; 82 % nss</td>
</tr>
<tr>
<td>68-70</td>
<td>40 % ss; 60 % nss</td>
</tr>
<tr>
<td>71-76</td>
<td>33 % ss; 67 % nss</td>
</tr>
<tr>
<td>77; 79-82</td>
<td>65 % ss; 35 % nss</td>
</tr>
</tbody>
</table>

Table 5: a) Averaged aerosol composition measured at Kaashidoo during the INDOEX campaign [Lelieveld, et al., 2001] and b) typical sea salt aerosol composition [Shettle and Fenn, 1976]. c) describes the MBL mixing between a) and b) assumed in the model.
The average daily measurements of the AOD [Welton et al., 2002] were used. The diurnal variation in aerosol composition was not taken into account. Analysis using the LOWTRAN-7 parameterisation for several different types of aerosols indicates that changes in the aerosol composition within the range of that observed in INDOEX, have only a negligible effect on the photolytic radiation field in the MBL. This assumption is supported by comparing the measured single scattering albedo of 0.874 ± 0.028 at 500 nm for the INDOEX period at Kaashidoo island [Bush and Valero, 2002] and our calculated value of 0.882 for this region. For the whole campaign the single scattering albedo values varied between 0.882 for the most polluted case and 0.932 for the SH region encountered during the campaign.

The profile of the aerosol extinction, $\alpha(\lambda, z) \, [km^{-1}]$ was obtained by using the LOWTRAN-7 aerosol profiles [Shettle and Fenn, 1976] for different scenarios, but modifying them in the lowest 5 km of the troposphere in order to fit the measured AOD (Figure 23).

$$AOD(\lambda) = \int_{a}^{b} \alpha(\lambda, z) \, dz \quad (141)$$
Figure 23: Micropulse Lidar (MPL) average profiles for AOD=0.15, 0.30, 0.45, 0.6. All extinction coefficient profiles are a mixture between the measured and the smooth Lowtran-profile [Welton, et al., 2002].
Figure 23: Micropulse Lidar (MPL) average profiles for AOD=0.15, 0.30, 0.45, 0.6. All extinction coefficient profiles are a mixture between the measured and the smooth Lowtran-profile [Welton et al., 2002].

In situ measurements of the aerosol extinction coefficient with respect to height have been performed on board the RV Ronald H. Brown [Welton et al., 2002].
The measured photolysis frequencies shown in Figure 24, Figure 25, Figure 26, and Figure 27 are based on $2\pi$ sr, whereas the model results are for $4\pi$ sr. Therefore all measured photolysis frequencies for $4\pi$ sr should be approximately 5-7% higher to account for the upwelling flux caused by the reflection at the ocean surface.

Figure 24 shows the modelled photolysis frequencies $j(\text{O}(^1\text{D}))$ and $j(\text{NO}_2)$ for AOD varying between 0.0 and 0.6, versus sec(SZA). The results show that the influence of aerosols varies with the SZA. The $j(\text{O}(^1\text{D}))$ rate for AOD = 0.0 decreases up to 23% for AOD = 0.6 for sec(SZA) = 1, the relative effect decreases up to 39% for sec(SZA) = 2. The same behaviour is observed for $j(\text{NO}_2)$, for sec(SZA) = 1 the relative decrease is 17% and for sec(SZA) = 2 the relative decrease is 37%.
Figure 24: Modelled photolysis frequencies of $j(O(^1D))$ and $j(NO_2)$ for different AOD vs. sec(SZA).

The calculated $j$ values depend upon Rayleigh scattering ($\alpha_{\text{ray}}$), trace gas absorption ($\alpha_{\text{trace}}$), and Mie scattering ($\alpha_{\text{Mie}}$, i.e. aerosol scattering). The influences of these three effects are wavelength dependent. In general the $\alpha_{\text{ray}}$ and $\alpha_{\text{trace}}$ (e.g. $O_3$ and NO$_2$) are more important in the short wavelength region and $\alpha_{\text{Mie}}$ becomes more
significant in the longer wavelength region. Therefore, the relative influence of aerosols on the photolysis frequencies, as measured by the ratio \( j(\text{AOD}=0.0)/j(\text{AOD}=0.6) \), which varies with \( \sec(\text{SZA}) \), is higher at longer wavelengths. Thus \( j(\text{NO}_2) \), which is weighted towards 400 nm is expected to be more influenced by the presence of significant amounts of aerosol than \( j(\text{O}(^1\text{D})) \), which is weighted towards 300 nm.

In Figure 25, the correlation of simulated and measured \( j(\text{O}(^1\text{D})) \) is plotted separated into different AOD regimes. Overall the agreement is reasonable, but in general the calculated \( j \) values underestimate the measured photolysis frequencies when lower AODs are present. This leads to differences of up to 11% for the lowest aerosol loading observed during the campaign. This effect is most probably caused by the assumed climatology profile of the trace gases, which is not representing the encountered situation correctly. However, even if we use a profile in the model that represents the low aerosol cases, we cannot reproduce the decreasing effect of the aerosols on the photolysis frequencies. The model accounts only for a decrease in \( j(\text{O}(^1\text{D})) \) by aerosols of 10% (AOD 0.1 to 0.4, SZA 20°, see Figure 24), whereas the measurements show a decrease of 33% for DOY 57 (SZA 20°, AOD 0.1) compared to DOY 68 (SZA 20°, AOD 0.4).

![Figure 25: Correlation between measured and modelled \( j(\text{O}(^1\text{D})) \) photolysis rates during INDOEX, separated into different AOD ranges.](image-url)
Figure 26 shows j(NO$_2$) versus local solar time for different conditions: clean maritime air above the Indian Ocean, polluted air above the Indian Ocean and polluted air over the eastern US for comparison. Figure 27 is similar to Figure 26 but plotted versus sec(SZA). The comparison between measured and modelled j(NO$_2$) show a good agreement for the low aerosol case (DOY 57), but the high aerosol case (AOD = 0.4) is overestimated by the model, even for AOD 0.6. Again the model cannot account for the influence of the aerosol on the photolysis rate. It appears that the absorption of aerosols in the UV is not well parameterised in the LOWTRAN-7 algorithm [Burkert et al., 2003c]. Within this context, Jacobson [1999] hypothesized the absorption of nitrated and aromatic aerosol components and nitrated aromatic gases can play a significant role in the attenuation of the ultraviolet irradiances. In contrast to Figure 25, Figure 26 and Figure 27 show, that j(NO$_2$) for the low aerosol case is well described in the model, whereas the high aerosol case is overestimated by ~ 15%. This different behaviour indicates an inaccurate model parameterisation in the wavelength behaviour of the absorption and/or scattering of the aerosols and/or absorption of nitrated aromatic gases [Jacobson, 1999].
Figure 26: Diurnal variation in the photolysis rate coefficient for NO₂; only cloud-free data are shown. Filled squares (measurements) and the black curve (model) represent data from the clean, marine atmosphere on DOY 57 at 4°S with an AOD of about 0.07 at 500 nm. Open squares (measurements) and grey curve (model) represent data from a polluted atmosphere over the northern Indian Ocean on DOY 65 at 6°N with an AOD of 0.4 at 500 nm. Crosses represent data from the polluted atmosphere over the Eastern US (Greenbelt, Maryland, 39°N) on July 15, 1995 with an AOD of 0.88 at 520 nm and 1.4 at 380 nm.
Figure 27: The same data as Figure 26, but with the photolysis rate coefficients plotted as a function of the secant of the solar zenith angle. Filled squares (measurements) and black curve (model) represent data from the clean marine environment; Crosses represent data from a polluted environment over North America, and open squares (measurements) and grey curve (model) represent data from a polluted environment in the Northern Indian Ocean.

Clearly the polluted Indian Ocean air appears to be the most severely impacted by the presence of aerosols. Particles with a low single scattering albedo ($\omega$), as were encountered downwind of India, are more effective at reducing the rate of NO$_2$ photolysis (and the rate of O$_3$ production) than are particles having a single scattering albedo near unity, which is the normal situation, encountered over the eastern US. This is especially true for small solar zenith angles (near solar noon) when enhanced scattered radiation from particles with a high $\omega$ compensates for losses in the direct beam. Comparing the j(NO$_2$) model results with the measurements in Figure 27 shows that the weaker variation with the sec(SZA) for the INDOEX data is well reproduced in the model. Therefore the assumed aerosol composition seems reasonable, only the total amount of absorption by the aerosols is not in agreement with the measured results.
4.2.3.2 Interpretation of the MBL chemistry

The chemistry of the MBL during INDOEX was simulated constraining the model to the measurements of trace gases and conditions described above. In more detail, the species, DMS [Wisthaler et al., 2002], H$_2$ (500 pptv), O$_2$ (21 %), N$_2$ (78 %), CH$_4$ (1.8 ppmv NH, 1.7 ppmv SH), CO$_2$ (350 ppmv), NMHC (i.e. C$_2$H$_6$, C$_3$H$_8$, C$_2$H$_2$, C$_2$H$_4$, C$_3$H$_6$) were held constant in the model. The trace gases, C$_2$H$_2$, C$_2$H$_4$, and C$_3$H$_6$ were fixed to the values measured by [Jens Mühle, personal communication, 2002] and are shown in Table 6.

<table>
<thead>
<tr>
<th></th>
<th>C$_2$H$_4$</th>
<th>C$_3$H$_6$</th>
<th>C$_2$H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHmT</td>
<td>48</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>NHcT</td>
<td>62</td>
<td>22</td>
<td>200</td>
</tr>
<tr>
<td>NHcX</td>
<td>60</td>
<td>23</td>
<td>250</td>
</tr>
<tr>
<td>NHmT</td>
<td>66</td>
<td>22</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 6: Assumed mixing ratios for C$_2$H$_4$, C$_3$H$_6$, and C$_2$H$_2$ separated into different air mass regions [according to Jens Mühle, personal communication, 2002]

These values can only be treated as rough estimates as the probes were partly contaminated by the building up of alkenes due to the long storage time of the canisters [for details Mühle et al., 2002]. The concentrations can be assumed as upper limits compared with literature values [Singh and Salas, 1982, Duce et al., 1983, Heikes et al., 1996]. However, sensitivity studies have shown that the concentration of these species have a negligible influence on the RO$_2^*$ and HCHO model results. The mixing ratios of H$_2$O, CO, O$_3$, HCHO [Wagner et al., 2002], and CH$_3$OH [Wisthaler et al., 2002] were initialised each day with the measured values at 0 UTC. For the trace gases not measured during the cruise, the following values were used for initiation of the photochemistry: H$_2$O$_2$ (1000 pptv), and CH$_3$O$_2$H (400 pptv). The photolysis frequencies were initialised every 10 min with the values calculated by the PHOTOST model. The model results were scaled to the measured j(NO$_2$) and j(O(^1)D)), including the correction for the reflected radiance. No dynamic processes were considered in the box model. Reasonable agreement between simulated and measured trace gases was achieved on most of the days. The analysis of the results highlights the following interesting features:
4.2.3.2.1 RO$_2^*$ diurnal variation

Figure 28 shows the averaged diurnal behaviour for the measured and modelled RO$_2^*$ mixing ratios for the NH and SH. A clear early morning and late afternoon bulge of RO$_2^*$ is observed: The maximum of RO$_2^*$ being around local noon (~UTC + 4 hrs).

![Figure 28: Average diurnal variation of measured and modelled RO$_2^*$ mixing ratios for the NH and SH during INDOEX. Local time is given by UTC + ~4 hrs.](image)

The chemical simulations were performed with two different input values comprising the reported NO for the NH and the SH. In order to achieve reasonable NO behaviour, the NO$_2$ mixing ratio was fixed to either 0 or 10 pptv. In the 10 pptv case, the photodissociation of NO$_2$ and the reactions between NO, O$_3$, and NO$_2$ lead to a diurnal variation of NO with maximum mixing ratios around noon, varying between ~5-8 pptv. Any variation of NO$_2$ can be neglected, because its reactions are of minor importance for RO$_2^*$ under the investigated conditions.

The averaged maximum RO$_2^*$ mixing ratio, occurring within two hours of local noon, is reasonably well simulated in both hemispheres within the experimental error. Maximum mixing ratios are reached at solar noon. In the SH air masses, the CO mixing ratios are lower than those in the NH air masses, while the amount of CH$_4$, the dominant hydrocarbon is about the same (SH ~ 1.7 ppmv, NH ~ 1.8 ppmv). As a result, the rate of
conversion of OH to HO\textsubscript{2} is reduced and relative to the amount of HO\textsubscript{2} more RO\textsubscript{2}, i.e., only organic peroxy radicals without HO\textsubscript{2} are produced. These effect result in the ratio of RO\textsubscript{2} to HO\textsubscript{2} being higher in the SH than in the NH. When small amounts of NO are added to clean NH or SH air in the model, the relative effect in the RO\textsubscript{2}\textsuperscript{*} mixing ratio is larger in the SH, because the ratio of RO\textsubscript{2} to HO\textsubscript{2} is larger in the SH than in the NH. A variation of the fixed input NO\textsubscript{2} mixing ratios in the model between 0 and 10 pptv leads to differences in the maximum RO\textsubscript{2}\textsuperscript{*} mixing ratios at noontime up to 20\% in the SH and up to 10\% in the NH.

The modelled local noontime averaged ratio of RO\textsubscript{2}/HO\textsubscript{2} without NO\textsubscript{x} chemistry is about 2 for the NH and 3 for the SH. In the model run with 10 pptv NO\textsubscript{2} the ratio decreases to ~1.6 for the NH and ~1.8 for the SH.

A non negligible nocturnal signal of RO\textsubscript{2}\textsuperscript{*} varying between 5 and 10 pptv is observed on most of the days. In contrast the RO\textsubscript{2}\textsuperscript{*} signal decreases to values below the detection limit and close to zero during the occasional rain periods observed during INDOEX. Similar nocturnal signals have been observed previously in the MBL [Burkert et al., 2001b, Andrés-Hernández et al., 2001] and their potential origin has been discussed. According to model investigations, a nocturnal RO\textsubscript{2}\textsuperscript{*} signal of no more than ~ 3 pptv can be explained. The expected amounts of NO\textsubscript{3} in such remote regions are too low to lead to significant production of RO\textsubscript{2}\textsuperscript{*} through the reactions of NO\textsubscript{3} with VOC during the night. Significant production of radicals by the ozonolysis of alkenes or biogenic species seems also unlikely. The isoprene mixing ratio observed by Yokouchi et al. [1999] was generally below 10 pptv above the northern Indian Ocean. This low amount cannot significantly contribute to the production of OH during the night. The ozonolysis of alkenes is also assumed to be negligible due to the low concentrations of light NMHC observed in remote marine regions [Koppmann et al., 1992]. A long lived RO\textsubscript{2} may explain the observed behaviour but its presence is questionable. Such radicals left over from daytime would anyway give decreasing concentrations during nighttime, contrary to the plateau-like signal that is observed.

A likely explanation for the nighttime maritime residual signal of RO\textsubscript{2}\textsuperscript{*} lies in the sensitivity of the PERCA towards ClO\textsubscript{x} (Cl+ClO+OClO), reported by Perner et al. [1999]. The chain length measured in a PERCA of identical construction to that used during INDOEX has been estimated to be ~300 for dry conditions. As a result the PERCA is about 10 times more sensitive to OClO/ClO than to RO\textsubscript{2}\textsuperscript{*} under the high humidity conditions encountered during the INDOEX campaign, provided that this
chain reaction is independent of H$_2$O. Assuming that this is the origin of the nighttime signal an upper limit of the nighttime ClO/OCIO mixing ratio of between 0.3 and 1 pptv is estimated.

There is an ongoing discussion about the presence of halogens in the troposphere. Several mechanisms have been proposed which yield Br$_2$, BrCl and possibly Cl$_2$ from inorganic reactions of acidic aerosols [Sander and Crutzen, 1996]. Br$_2$, BrCl and Cl$_2$ are photolysed during daytime and the resulting Br and Cl atoms react with O$_3$ to form ClO and BrO. ClO reacts with BrO to form OCIO. During the day OCIO is photolysed but at night it is long lived. Thus the daytime production of relatively small amounts of BrO and ClO might lead to small but significant amounts of OCIO at night. No ClO$_x$ measurements were performed during INDOEX. The presence, however, of photochemically produced halogen oxides, in particular iodine oxide in the MBL has been indicated recently by measurements at Mace Head, Ireland [Carpenter et al., 1999].

In early morning and late afternoon the modelled and observed RO$_2^*$ are significantly different. Figure 28 shows that the measured curves of RO$_2^*$ are clearly broader than the simulated diurnal cycles. This effect is less pronounced for the SH. Previous campaigns in the MBL above the Atlantic Ocean have not revealed so clearly such behaviour [Burkert et al., 2001b, Andrés-Hernández et al., 2001].

The production of RO$_2^*$ appears to start earlier in the morning and continues longer in the later afternoon than in the model. The broad shape of the RO$_2^*$ diurnal evolution is most pronounced in air parcels originating from India and the Bay of Bengal (see Figure 29). This effect is not correlated with the appearance of higher amounts of NMHC (see Figure 22), but rather with higher amounts of CO, acetone, and HCHO.
Figure 29: Modelled and measured average diurnal behaviour of RO$_2^*$ mixing ratios for different air mass regions during INDOEX. Note: absolute concentrations of measurements and model are in good agreement, but the observations are broader.
Figure 29: Modelled and measured average diurnal behaviour of \( \text{RO}_2^* \) mixing ratios for different air mass regions during INDOEX. Note: absolute concentrations of measurements and model are in good agreement, but the observations are broader.
Possible explanations for the broad shape behaviour or bulge in the morning and evening of the \( \text{RO}_2^* \) are as follows:

1) **Unidentified VOC:** The presence of an “as yet” unidentified VOC having faster reactions rates with OH than either CH\(_4\) and CO, leading to \( \text{RO}_2^* \) radicals other than \( \text{HO}_2 \) and CH\(_3\)O\(_2\). The \( \text{RO}_2 \) additional radical loss reactions also need to be slow compared to the \( \text{RO}_2 \) reactions considered in the model. This combination of effects would explain the shape of the curve in the early morning and in the evening, but not the flatter plateau at midday.

   This further requires that the diurnal variation of this as yet unknown NMHC has a minimum around noon. This implies a short photochemical lifetime, which would prevent such compounds from reaching the open ocean, if emitted by continental sources.

   Should such a NMHC be emitted from the ocean, the observed NH/SH difference in the \( \text{RO}_2^* \) diurnal behaviour could not readily be explained. Similarly the requirement of having a large source of NMHC is somewhat in conflict with such a compound having a short photochemical lifetime.

2) **Radical Reservoir:** The presence of a radical reservoir substance, which photolysis in the early morning, produces higher amounts of \( \text{RO}_2^* \). This is most likely to be a reservoir for \( \text{HO}_2 \) radicals i.e. XHO\(_2\).

   \[
   X + \text{HO}_2 \rightarrow \text{HOOX}
   \]

   \[
   \text{HOOX} + h\nu \rightarrow X + \text{HO}_2
   \]

   The additional reaction of \( \text{HO}_2 \) with \( X \) would lead to smaller amounts of \( \text{RO}_2^* \) radicals around midday and explain the plateau observed. The consequent reduction of the \( \text{HO}_2/\text{CH}_3\text{O}_2 \) ratio implies an increasing lifetime for \( \text{CH}_3\text{O}_2 \) in the evening, which could partly account for the measured nighttime signal. This effect would be more pronounced in the NH due to the higher \( \text{HO}_2/\text{CH}_3\text{O}_2 \) ratio, which is a consequence of the higher CO/\( \text{CH}_4 \) ratio in the NH as compared to the SH.

3) **Bromine and Iodine:** The presence of the halogen oxides BrO or IO would mean that Br and I atoms are present. These react rapidly with alkenes, alkynes, and aldehydes but not with alkanes. This is, however, an unlikely source of sufficient early morning or late afternoon \( \text{RO}_2^* \) to explain the bulge. These halogen oxides do
react rapidly with both HO$_2$ and RO$_2$ and form HOBr and HOI respectively. In the
gas phase it is unlikely that sufficient HOBr or HOI is present to explain the bulge
in RO$_2^*$, because this would require relatively large amounts of BrO or IO which
would remove O$_3$.

The presence of halogenoxides like BrO, which react with HO$_2$ as described
in the reactions (48),(49), and (50)), leads to a loss of RO$_2^*$. However, the amounts
of halogens needed for the reservoir would unrealistically influence other species,
e.g. BrO mixing ratios in the range of a few ppbv would destroy all O$_3$ present in the
MBL.

$$Br + O_3 \rightarrow BrO + O_2$$

(48)

$$BrO + HO_2 \rightarrow BrOH + O_2$$

(49)

$$BrOH + h\nu \rightarrow Br + OH$$

(50)

4) **Chlorine.** The presence of only small amounts of Cl leads to the oxidation of all
VOC, alkanes, alkenes alkynes and thus to an increase of RO$_2$ radicals. This
possible explanation of the bulge in RO$_2^*$ is consistent with the observations of
relatively large amounts of HCHO during INDOEX [Wagner et al., 2001, 2002].
The nighttime signal of the PERCA additionally provides indirect evidence for the
presence of OCIO/ClO/Cl in the MBL [Burkert et al., 2001b]. The largest nighttime
signals are in regions where the bulge in the diurnal evolution of RO$_2^*$ is most
pronounced.

The presence of both chlorine and bromine is predicted to come from sea salt
aerosols by the MOCCA model [Sander and Crutzen, 1996, Dickerson et al., 1999,
Vogt et al., 1996]. Interestingly the diurnal behaviour of Cl is different from that of
Br: Cl having a maximum in the early morning and late afternoon as required to
explain the RO$_2^*$ bulge.

The diurnal evolution of Cl, inferred from the RO$_2^*$ observations required to explain
the missing source of RO$_2^*$, is described in Figure 30. This is similar to and in
agreement with the diurnal behaviour simulated and predicted by the MOCCA
communication, 2002].
Figure 30: The required diurnal behaviour of Cl to describe the observed broad shape in the measured RO\textsubscript{2}^\textsuperscript{*} diurnal behaviour.

In recent years there has been discussion about the possible presence of a source of Cl in the planetary boundary layer [Singh et al., 1983, Cicerone, 1981, Finlayson-Pitts, 1993, Graedel and Keene, 1995, Vogt et al., 1996, Moore et al., 1996, Spicer et al., 1998, Yokouchi et al., 2000, Rhew et al., 2000, Keppler et al., 2000]. The largest bulge in the diurnal behaviour of RO\textsubscript{2}^\textsuperscript{*} was observed in the air masses from India and the surrounding areas of the Bay of Bengal (NHcT). These air masses were characterised by moderate levels of acidity in the aerosols and a moderate nitrate to sulphate ratio [Ball et al., 2003]. The presence of small amounts of NO in these air masses compared to the pristine MBL, would convert ClO to Cl via the reaction:

\[
NO + ClO \rightarrow Cl + NO_2
\] (142)

Thereby leading to the regeneration of O\textsubscript{3} via the photolysis of NO\textsubscript{2}, but enhancing the concentration of Cl. However, concerning the measurements of NO, again the NHcX air masses indicate slightly higher amounts compared to the NHcT air masses (see Figure 29).

The measurements of Cl\textsubscript{2} [Spicer et al., 1998] in a coastal region of the eastern USA showed high amounts of Cl\textsubscript{2} during the night, reaching levels up to 150
Photolysis in the early morning, therefore, produces Cl concentrations of the order of $1.3 \times 10^5$ atoms $\text{cm}^{-3}$ at maximum. The source of the inorganic Cl is presumably multi-phase reactions involving aerosols.

An alternative potential explanation for the presence of higher amounts of Cl in the NHcT regime is the enhanced emissions of halogenated carbon compounds such as CH$_3$Cl in coastal regions. The oxidation, proceeds as described in chapter 2.2.1.8.

Several studies [Khalil and Rasmussen, 1999, Moore et al., 1996] have shown that the ocean is not a significant source. However Yokouchi et al. [2000] observed up to 2100 pptv of CH$_3$Cl on islands in the tropics. It is not clear, whether these high mixing ratios are related to emissions from the forested land.

An upper limit of Cl mixing ratio generated from 2100 pptv of CH$_3$Cl can be calculated by a simple steady state assumption for Cl and the hypothesis that every CH$_3$Cl oxidised by OH leads to a Cl.

$$[\text{Cl}] = \frac{k_{\text{CH}_3\text{Cl}+\text{OH}} [\text{CH}_3\text{Cl}] [\text{OH}]}{k_{\text{Cl}+\text{CH}_4} [\text{CH}_4]} \quad (143)$$

This yields $[\text{Cl}] = 5.9 \times 10^3$ [atoms $\text{cm}^{-3}$], for an $[\text{OH}] = 1 \times 10^7$ [molecule $\text{cm}^{-3}$] and mixing ratio of CH$_4 = 1.8$ ppmv, i.e. apparently too small to explain the observed effect. In addition, the measurements of CH$_3$Cl onboard the citation plane during INDOEX only indicated amounts in the NHcT air masses of up to 750 pptv [Scheeren et al., 2002].

Overall, the nighttime RO$_2^*$ signals and the bulge in RO$_2^*$ appears to provide evidence for a source of Cl in the MBL, which maximises in the early morning. This source is most likely to comprise inorganic multiphase reactions on sea salt aerosol, but the oxidation of organic halides cannot be excluded.

**Contribution of Cl to the tropospheric oxidising capacity (OC) of CH$_4$**

The OC with respect to oxidation and consequent removal of a species from the marine boundary layer can be defined as the sum of the effective first-order reactive removal processes.

$$OC_{\text{CH}_4} = \int_{\text{day}} \left( k_{\text{OH}+\text{CH}_4} [\text{OH}] [\text{CH}_4] + k_{\text{Cl}+\text{CH}_4} [\text{Cl}] [\text{CH}_4] \right) dt$$

Assuming that the bulge in RO$_2^*$ results from Cl, and this indicates that above the Indian Ocean Cl accounts for up to ~8% of the average oxidising capacity of CH$_4$. A
daily integral was chosen to compare the OC of OH and Cl. The Cl diurnal profile was the same as presented in Figure 30.

**Comparison of the remote MBL above the Atlantic and Indian Ocean**

The average RO$_2^*$ behaviour from the measurements made in the NH and SH in the Atlantic Ocean are shown in Figure 31 and Figure 32. These measurements were made during the ALBATROSS campaign in 1996 [Burkert et al., 2001b] and AEROSOL in 1999, immediately prior to INDOEX with the same instrument [Andres-Hernandez et al., 2001]. The ALBATROSS cruise went aboard the Polarstern from Bremerhaven, Germany (54°N, 9°E) to Punta Quilla, Argentina (50°S, 67°W). Much of the voyage was around 30°W with the Polarstern travelling from North to South. In contrast the AEROSOL cruise went from Norfolk, Virginia (37°N, 76°W) to Cape Town, South Africa (34°S, 22°E), cutting across the North and South Atlantic Oceans.

![Figure 31: Average diurnal variation of measured and modelled RO$_2^*$ mixing ratios for the NH and SH during ALBATROSS (1996) above the Atlantic Ocean. Local time is given by UTC + ~2 hrs.](image)
Figure 32: Average diurnal variation of measured and modelled RO$_2^*$ mixing ratios for the a) NH and b) SH during AEROSOL (1999) above the Atlantic Ocean. Local time approximately UTC a) +4 hrs and b) +2 hrs.
Using the measured amounts of O₃ and related trace gases and neglecting any halogen chemistry, the model predicts similar concentrations of RO₂⁺ in both the NH and the SH in both 1996 and 1999: the noontime maximum mixing ratio of RO₂⁺ being around 36 pptv. In contrast the estimated amounts of RO₂⁺ in the northern and southern part so the Indian Ocean are significantly different.

The measurements from the Atlantic Ocean show for both the ALBATROSS and the AEROSOL campaign the following:

1) The broader shape behaviour is more pronounced in the NH than in the SH.
2) The noontime maximum of RO₂⁺ is small but significantly higher in the NH than in the SH.
3) The early morning increase of RO₂⁺ is not as fast as in the results from the Indian Ocean.
4) The broader shape in the Atlantic Ocean results appears similar to an offset throughout the day.
5) The nighttime unexplained signal is not considered to be an artefact of the PERCA, because during periods of rain the signal was observed to go zero both during the day and during the night.

The differences between the Atlantic and the Indian Ocean are most probably caused by the presence of higher amounts of NOₓ, CO, NMHC, and different meteorological conditions (i.e. higher MBL height in the Atlantic compared to the Indian Ocean). The diurnal behaviour of the O₃ mixing ratio above the Atlantic Ocean does not often show significant loss of O₃. This is another indication for production of O₃ from the higher amounts of NOₓ although the measurements above the Atlantic Ocean were performed far away from coastal regions. In addition, the difference in the O₃ mixing ratio between NH and SH was small above the Atlantic Ocean during the ALBATROSS and AEROSOL campaign.

The MBL of the remote Indian Ocean generally seems to be cleaner than the remote parts of the Atlantic Ocean visited on the research voyages and exhibits the cleanest air observed thus far in the SH. This may explain why the behaviour of the small amounts of halogens has a more pronounced effect on the RO₂⁺.
4.2.3.2.2 HCHO chemistry

The RO$_2^*$ and HCHO chemistry is closely related in the MBL. The production of alkoxy, RO, radicals from peroxy radicals leads to the production of aldehydes and ketones via the reactions of RO with O$_2$: the reaction of CH$_3$O with O$_2$ is expected to be the main source of HCHO in the remote MBL. The photolysis of HCHO is an additional significant source of HO$_2$ radicals in the MBL as compared with the reaction of OH with CO in the presence of O$_2$.

It has been reported in the past that measured HCHO concentrations in the MBL of the Atlantic Ocean are in disagreement with model results [Burkert et al., 2001b, Weller et al., 2000, and references therein]. This has been attributed to additional sources of non methane hydrocarbons e.g. from ship exhaust and biomass burning plumes crossing the ocean [Burkert et al., 2001b].

The HCHO expected in the MBL above the Indian Ocean was simulated using the chemical model and compared with the measurements performed during INDOEX. As for RO$_2^*$ simulations, the NO$_2$ was constrained to fixed amounts of either 0 or 10 pptv, which represent the minimum and maximum in the range of observations.

In regions exhibiting low CO values, the effect of NO$_x$ on the amount of HCHO is more pronounced due to the higher rate of conversion of RO$_2$ radicals to HO$_2$. As a result, the NO$_2$ values used in the model determine to a large extent the calculated HCHO mixing ratio. In Figure 33 the daily averages of measured and calculated HCHO mixing ratios are plotted. In spite of the uncertainty in the NO measurements mentioned above, the agreement is fair between measured and simulated HCHO, taking the experimental error into account. This is similar to the results obtained by Wagner et al. [2001].
In the period DOY 68-70 the simulated HCHO values are significantly larger than the measured amounts. This is similar to previous results [Liu et al., 1992, Jacob et al., 1996]. Some investigators have proposed that the heterogeneous chemistry in clouds or aerosols as being responsible for the fast loss of HCHO. On those days, where this behaviour is observed however, the AOD measured is lower than on previous days.

An alternative explanation of the low HCHO mixing ratios has recently been reported by Wagner et al. [2001]. For this explanation, the lower HCHO mixing ratios are interpreted to be an indication of the prevailing free tropospheric character of the subsiding air measured. The back trajectories of the air masses in this case, however, indicate that the air sampled on the days in question remained for at least two days in the MBL which is sufficient time for HCHO to achieve a stationary state.

The observed relationship between the daily maximum measured mixing ratios of CO, HCHO, and RO$_2^*$ confirm the close chemical link between these species. The model results cannot explain the extremely high concentrations of RO$_2^*$ observed during the DOY 64 and 65. Surprisingly during days with enhanced levels of NMHC (DOY 68-72) no enhanced RO$_2^*$ or HCHO mixing ratios are observed.

For enhanced CO levels (DOY 63-65) and maximum noontime RO$_2^*$ mixing ratios, the model does not reproduce the observed HCHO values. In the model higher
CO concentrations lead to higher HO\(_2\) and less OH. This results in a lower production rate of CH\(_3\)O\(_2\) via the oxidation of methane and also a higher loss rate as a result of the HO\(_2\) reaction with CH\(_3\)O\(_2\). The CH\(_3\)O\(_2\) loss reactions are the main source for HCHO. Under the assumption that all other radical sources do not significantly increase, then for higher CO concentrations it is difficult to explain the CO and HCHO correlation observed, because the opposite effect is predicted from the expected chemistry.

**Possible explanations of the HCHO behaviour:**

- A reaction of CO and OH in the presence of water producing HCHO via a complex mechanism e.g.

\[
\text{CO} + \text{OH} \rightarrow \text{COOH} \\
\text{COOH} + \text{H}_2\text{O} \rightarrow \text{HCHO} + \text{HO}_2
\]

However, this reaction is expected to be slow and is endoergic.

- A reaction of CO and HO\(_2\) catalysed by the presence of water, which produces OH and CO\(_2\). Some studies in the past have indicated that their reaction may occur but other have obtained a very low upper limit for this reaction rate coefficient [DeMore et al., 1997, and references therein]. However, an extended investigation concerning the influence of water on the reaction rate coefficient has not yet been done. A reaction of the described type would change the ratio between HO\(_2\) and OH and would also increase the amount of RO\(_2\) due to the higher amount of OH present. Such a reaction would lead via enhanced OH concentrations to an enhanced oxidation of hydrocarbons and rate of production of RO\(_2\) and consequently to a larger production of HCHO in the atmosphere.

- The presence of a NMHC, which has not yet been identified and included in the model having similar sources to CO. Its rate of oxidation needs to be in the same order of magnitude to that of CH\(_4\).

- The presence of another oxidising agent like OH for example Cl, which leads to additional amounts of RO\(_2\) and therefore higher concentrations of HCHO. This requires amounts of Cl to be in the order of 1x10\(^4\) to 1x10\(^5\) molec cm\(^{-3}\).

It is very interesting to note that recent measurements of the isotopic fractionation of CH\(_4\) above the Pacific Ocean have recently provided evidence for the enrichment of the CH\(_4\) fractions, which cannot be explained by OH chemistry alone. An additional oxidant is required [Allan et al., 2001].
In summary it is probably far from surprising that the broad shape behaviour of \( \text{RO}_2^* \) is coincidental with increased amounts of HCHO in the INDOEX measurements. The oxidation of \( \text{CH}_4 \) and for that matter any other NMHC, initiated by Cl would in pristine regions of the atmosphere yield additional HCHO, compared to that predicted from the OH initiated \( \text{CH}_4 \) and NMHC oxidation in the remote pristine atmosphere.

Finally assuming that the bulge in \( \text{RO}_2^* \) results from Cl, and this indicates that in the remotes and pristine Cl accounts for up to ~8% of the average oxidising capacity of \( \text{CH}_4 \) of the atmosphere.

### 4.2.4 Summary

A set of trace gases and photolysis frequencies has been successfully measured in the MBL above the Indian Ocean during the INDOEX campaign in February and March 1999. Air masses with different trace gas mixing ratios and origins have been encountered and analysed.

The photolysis frequencies at the ground level were calculated using an RTM and compared with measured values. The model was initialised with the measured AOD profiles and aerosol composition. The \( \text{j(O}^1\text{D}) \) and \( \text{j(NO}_2 \) calculated photolysis frequencies at 30° SZA for AOD of 0 and 0.6 differ by about 30% and 24% respectively.

A box homogenous gas phase chemistry model has been used to simulate the chemistry of the MBL and its results compared with the trace gas and radical measurements. The diurnal behaviour of the measured \( \text{RO}_2^* \) is observed to be significantly broader than that estimated using an OH oxidation scheme suitable for the pristine and remote MBL. This broad \( \text{RO}_2^* \) or bulge behaviour indicates that more \( \text{RO}_2^* \) is present in the early morning and late afternoon than OH chemistry predicts.

The presence of the broader \( \text{RO}_2^* \) behaviour is not correlated with the amount of NMHC but can be related to the origin of the air masses. Overall this behaviour indicates the presence of missing chemistry in the model in the early morning and late afternoon. One reasonable explanation of the observed behaviour is the presence of small amounts of chlorine in the MBL. The sources of Cl are most likely to be the release from aerosols and also possibly the oxidation of organic halides.
The agreement between the modelled and measured HCHO is reasonable taking the experimental error and the uncertainty of NO measurements into account. The observed relationship between the daily measured maximum mixing ratios of CO, HCHO, and RO$_2^*$ indicates a close chemical link between these species, which cannot be well explained by the known OH oxidation chemistry used in the box model. The most likely explanation of this behaviour is the presence of Cl in the MBL, as proposed above.

Overall the measurements of trace gases and radicals, obtained aboard the R.V. Ronald H. Brown during INDOEX have provided the first detailed observations of the chemistry of the remote marine boundary layer above the Indian Ocean. The observed RO$_2^*$ is not that expected for OH initiated hydrocarbon oxidation. Evidence is presented which indicates that Cl contributes significantly to the oxidative capacity of the tropical MBL. To gain confidence about the proposed explanation of the RO$_2^*$ behaviour, research campaigns focusing on the identification of halogen oxide radicals in the MBL are required.
4.3 Photochemistry and radiative effects of aerosols

4.3.1 Introduction

For this study measurements of in situ and vertical profiles of $O_3$ were taken above the Indian Ocean. These measurements were enlarged by satellite observations of excess $O_3$, total NO$_2$, total HCHO, and lightning produced NO$_2$. These measurements were part of INDOEX [Lelieveld et al., 2001a, 2001b, Ball et al., 2003, http://www-indoex.ucsd.edu].

The main objective of this study is to understand the fast photochemistry of $O_3$ in the MBL, in particular the production and loss mechanisms responsible for the diurnal behaviour of $O_3$, together with a qualitative estimate of the influence of transport on these mechanisms. Special attention was given to the advective and convective processes [de Laat et al., 2000, 2001a, 2001b] and the MBL behaviour. The MBL behaviour is discussed in context with the presence of aerosols and their effect on stabilising the atmosphere by absorbing the direct sunlight [Kinne and Pueschel, 2001, Jacobson, 1998b, Gamazayachikov et al., 1998, Kiehl et al., 1999]. Aerosols also have an impact on the UV actinic flux and therefore on $O_3$ [Burkert et al., 2002, Dickerson et al., 1997, Liao et al., 1999, Kondragunta, 1997].

Measurements in the southern Indian Ocean are used to analyse the different contributions of sources responsible for $O_3$ in remote areas.

4.3.2 Results

4.3.2.1 Characteristics of the different air masses observed

The four different air masses exhibited the following characteristics:

**SHmE (observed during DOY 54-58, 78.25-79.5)**

The SHmE regime showed the lowest mixing ratios for most trace species and in this sense was the least polluted air encountered. The maximum $RO_2^*$ mixing ratio during DOY 54-58 decreased with decreasing latitude from 35 to 25 pptv. The $O_3$
mixing ratio revealed the same behaviour, decreasing from 15 to 8 ppbv. The loss of O\textsubscript{3} per latitude decreases with decreasing latitude. The mean CO mixing ratio was 56 ppbv, the daytime average NO mixing ratio was below the detection limit of around 3 pptv. The NMHC mixing ratios were the lowest observed during the whole campaign. The mean values were: ethane 194 pptv, propane 7 pptv, and acetylene 21 pptv [Muehle et al., 2002]. The vertical profiles of O\textsubscript{3} mixing ratio showed a weak positive gradient with increasing altitude up to 12 km between 12°S and the ITCZ, where the O\textsubscript{3} reached levels about 40 ppbv [Hermann Smit, personal communication, 2001].

**NHmE (observed during DOY 76-78.25, 79.5-81)**

In the NHmE regime the CO and O\textsubscript{3} mixing ratios were around 90 ppbv and approximately 10 ppbv, respectively. The maximum RO\textsubscript{2}* mixing ratio varied between 55-60 pptv. The back-trajectories indicate a long travel time of the air parcel along the west-coast of India but staying over the ocean. The NO mixing ratio was below the detection limit (<5 pptv). Most of the NMHC doubled their mean mixing ratios compared to the SHmE air mass: ethane 332 pptv, propane 10 pptv, and acetylene 44 pptv. The vertical profiles of O\textsubscript{3} in this regime indicate an even weaker positive gradient in altitude compared to the SHmE regime, reaching levels of about 30 ppbv at 12 km.

**NHcT (observed during DOY 63-66, 74-76, 85-89):**

The NHcT regime was characterised by the highest observed maximum mixing ratios in RO\textsubscript{2}* and CO during the whole campaign. Maximum levels of up to 90 pptv RO\textsubscript{2}* and 200 ppbv CO were observed. NO measurements were higher than in the SHmE, but still close to the detection limit, around 6 pptv. The O\textsubscript{3} mixing ratios showed strong diurnal variations, with O\textsubscript{3} losses during the day being as large as 50%. The latitudinal gradient in O\textsubscript{3} was ~ 1.25 ppbv/°latitude heading North. The NMHC main mixing ratios increase for ethane up to 403 pptv, propane to 20 pptv, and acetylene to 133 pptv. The vertical O\textsubscript{3} profiles revealed an enriched layer between 1-3 km having mixing ratios larger than 70 ppbv. The upper level O\textsubscript{3} values were different depending on the periods of observation. Back-trajectory analysis indicate that the air masses originated over India and the Bay of Bengal. The NHcT regime also appeared to contain high concentrations of ash, soot, and other organic matter [Dickerson et al., 2002, Neusüß et al., 2002, Quinn et al., 2002]. This is evidence for heavy contamination by fossil fuel combustion, biomass burning, and wind-blown dust [Ball et al., 2003, Quinn
et al., 2002, Stehr et al., 2002]. The black carbon from India is currently considered to result mainly from internal combustion engines, biomass burning, and small-scale coal combustion. However, estimates of black carbon emissions from India yield much smaller values than do in situ observations. This suggests an additional source not yet considered, or, unusually high emissions factors [Dickerson et al., 2002]. Therefore considerable uncertainty remains about the sources and/or emissions.

**NHcX (observed during DOY 66-74)**

The NHcX regime was characterised by the highest observed concentration of O\textsubscript{3} and NMHC at the most northerly point of the whole campaign. O\textsubscript{3} mixing ratios reached levels up to 53 ppbv and the NMHC averaged mixing ratios were: ethane 927 pptv, propane 133 pptv, and acetylene 169.3 pptv. The latitudinal gradient in O\textsubscript{3} remained ~ 1.25 ppbv/°latitude heading North. RO\textsubscript{2} and CO varied weakly around 55 pptv and 122 ppbv respectively. NO mixing ratios reached their highest values of the campaign being approximately 9 pptv. The vertical profile in O\textsubscript{3} showed the same behaviour as in the NHcT regime with an O\textsubscript{3} enriched layer above the MBL. Back-trajectories indicate that the air masses originated over the Arabian Peninsula.

**4.3.2.2 Measurements of trace constituents and parameters**

**4.3.2.2.1 O3 in situ measurements**

The O\textsubscript{3} mixing ratio was measured successfully between DOY 54 and DOY 89. The three legs are presented in Figure 34 and the air masses encountered are labelled in the header. During the first leg the daily averaged O\textsubscript{3} concentration decreased while heading North to the ITCZ. In the course of the second and third leg the daily averaged O\textsubscript{3} concentrations varied strongly depending on the distance from the sources and the latitude. In the clean MBL, however, similar O\textsubscript{3} levels (24 hrs average) seem to correspond to the same latitudinal position.

In order to calculate the O\textsubscript{3} gradient per latitude, the O\textsubscript{3} gradient was calculated for the positions more at the South and the North of leg 2, i.e. DOY 65 (6°N, 35 ppbv)/73 (7°N, 35 ppbv) which have similar O\textsubscript{3} concentrations and DOY 70 (18°N, 50 ppbv). The difference is calculated considering the O\textsubscript{3} maximum of DOY 65, 70, and 73. The resultant gradient is ~1.25 ppbv/°latitude in O\textsubscript{3} heading North.
Similarly in the SH a comparison is possible between DOY 75 (3°N, 25 ppbv) and 78 (10°S, 10 ppbv) and between 78 with 82 (4°N, 30 ppbv), i.e. there is a decrease of 15 ppbv going to the South and an increase of 20 ppbv going to the North. This average leads to a gradient of ~1.25 ppbv/°latitude in O$_3$ heading North.

The gradient in the SH between DOY 55 (12°S, 14 ppbv) and 57 (5°S, 9 ppbv) is about 0.7 ppbv/°latitude in O$_3$ heading South. The latitudinal gradient in O$_3$ in the SH seems to be decreasing while heading towards the ITCZ as expected because the loss reactions of O$_3$ are dependent on the amount of O$_3$ itself. However, in the NH the gradient appears to be constant, which is in disagreement with the theory.

The O$_3$ diurnal variation within the MBL during INDOEX is characterised by a daytime depletion (around 10-50%) [Stehr et al., 2002], and a clear nocturnal recovery. The short term variations of O$_3$ seem to be superimposed on the latitudinal gradient described above.
Figure 34: Plots of the individual diurnal variation of \( \text{O}_3 \) and CO observed on legs 1 to 3 of INDOEX. The classification of the air masses encountered are written above the days, and vertical lines separate the different types of air masses.
4.3.2.2 O₃ soundings

In this section the cross sections for all O₃ soundings performed during the ship cruise are presented. They are grouped to represent more clearly the latitudinal behaviour of the vertical profiles. In Figure 35 the O₃ soundings are plotted from 0 to 5 km to more clearly illustrate the boundary layer structure. Figure 36 shows the complete series of cross sections (0 to 20 km).

In the NH a clear structure in the O₃ vertical distribution is observed. The lowest first kilometre also has the lowest O₃ mixing ratios (see Figure 35, leg 2 a-c, and leg 3). Directly above the MBL between 1 and 3 km there is a highly enriched O₃ layer, which is linked with high amounts of aerosols. In addition this layer is in most cases extremely dry. This is especially true during leg 3 within the 1 to 3 km layer O₃ mixing ratios reaching levels up to 80 ppbv, whereas the maximum O₃ mixing ratio in the MBL (0-1km) remained around 20 ppbv. During leg 1 and leg 2 d-e the vertical O₃ gradient was weaker and the O₃ mixing ratios increased evenly in relation to increasing height.
Figure 35: O₃ soundings (0 to 5 km) grouped into a) leg 1 (23-28 Feb.), b) leg 2 (5-10 March), c) NH leg 2 (11-13 March), d) leg 2 (13-14 March) days with same latitude, e) leg 2 (14-19 March), f) leg 2 (19-22 March), g) leg 3 (26-30 March) [H.G.J. Smit, Research Centre Jülich (ICG 2), Germany].
Figure 35: O3 soundings (0 to 5 km) grouped into a) leg 1 (23-28 Feb.), b) leg 2 (5-10 March), c) NH leg 2 (11-13 March), d) leg 2 (13-14 March) days with same latitude, e) leg 2 (14-19 March), f) leg 2 (19-22 March), g) leg 3 (26-30 March) [H.G.J. Smit, Research Centre Jülich (ICG 2), Germany].
INDOEX 1999: $\text{O}_3$ ppbv Cross section Leg 2 d (14 - 19 March 1999)
Obtained from Ozone/Humidity Soundings from RV "Ronald H. Brown"

Figure 35: $\text{O}_3$ soundings (0 to 5 km) grouped into a) leg 1 (23-28 Feb.), b) leg 2 (5-10 March), c) NH leg 2 (11-13 March), d) leg 2 (13-14 March) days with same latitude, e) leg 2 (14-19 March), f) leg 2 (19-22 March), g) leg 3 (26-30 March) [H.G.J. Smit, Research Centre Jülich (ICG 2), Germany].
Figure 35: $O_3$ soundings (0 to 5 km) grouped into a) leg 1 (23-28 Feb.), b) leg 2 (5-10 March), c) NH leg 2 (11-13 March), d) leg 2 (13-14 March) days with same latitude, e) leg 2 (14-19 March), f) leg 2 (19-22 March), g) leg 3 (26-30 March) [H.G.J. Smit, Research Centre Jülich (ICG 2), Germany].

In Figure 36 some macro-scale phenomena can be seen. During leg 1 the ITCZ can be identified at around 3°S, with low levels of $O_3$ being pumped upwards toward the tropopause. At the most southern soundings (~15°S) higher amounts of $O_3$ are observed in the mid-troposphere. The back trajectories for the 500 hPa niveau (Figure 37) show that air masses travelled for at least six days over the open ocean far away from any source region. There was also no evidence for lightning induced $O_3$ production (Figure 40, Figure 41). Back trajectories indicate that the air masses were originated at approximately 200 mbar. Therefore, it seems most likely that this air mass has stratospheric origin. This assumption is further supported by relative humidity data [http://saga.pmel.noaa.gov/indoex/rsonds/index.html] which show extremely low values (below 10%) between 3 and 8 km altitude.
In the past, stratospheric layers just below the tropopause have been repeatedly observed all over the Indian Ocean. Zachariasse et al. [2000] suggest that the extra tropical stratosphere feeds O$_3$ to the tropical troposphere from the NH and SH. The typical tropical and extra tropical O$_3$ vertical profiles indicate that decreasing tropopause height and the presence of the Subtropical Jetstreams at the transition zone between tropical and extra tropical hemispheres can lead to the intrusion of stratospheric O$_3$ into the troposphere [Zachariasse et al., 2000]. This assumption is supported by the potential vorticity maps for this region. On the way downward the stratospheric O$_3$ is diluted into the whole troposphere.

The presence of a strictly layered mid-tropospheric O$_3$ maximum in the NH and its correspondence with high amounts of absorbing aerosols leads to the conclusion that O$_3$ does not originate in the stratosphere [Zachariasse et al., 2000, Welton et al., 2002]. Under the assumption that the STE in the NH and SH is similar, and the observed SH vertical O$_3$ profiles are not influenced by anthropogenic sources, the differential profile between NH and SH must be equal to the anthropogenic influence in the tropics of the NH.
Figure 36: $O_3$ soundings (0 to 20 km) grouped into a) leg 1 (23-28 Feb.), b) leg 2 (5-10 March), c) NH leg 2 (11-13 March), d) leg 2 (13-14 March) days with same latitude, e) leg 2 (14-19 March), f) leg 2 (19-22 March), g) leg 3 (26-30 March) [H.G.J. Smit, Research Centre Jülich (ICG 2), Germany].
Figure 36: \(O_3\) soundings (0 to 20 km) grouped into a) leg 1 (23-28 Feb.), b) leg 2 (5-10 March), c) NH leg 2 (11-13 March), d) leg 2 (13-14 March) days with same latitude, e) leg 2 (14-19 March), f) leg 2 (19-22 March), g) leg 3 (26-30 March) [H.G.J. Smit, Research Centre Jülich (ICG 2), Germany].
Figure 36:  

O$_3$ soundings (0 to 20 km) grouped into a) leg 1 (23-28 Feb.), b) leg 2 (5-10 March), c) NH leg 2 (11-13 March), d) leg 2 (13-14 March) days with same latitude, e) leg 2 (14-19 March), f) leg 2 (19-22 March), g) leg 3 (26-30 March) [H.G.J. Smit, Research Centre Jülich (ICG 2), Germany].
Figure 36: O₃ soundings (0 to 20 km) grouped into a) leg 1 (23-28 Feb.), b) leg 2 (5-10 March), c) NH leg 2 (11-13 March), d) leg 2 (13-14 March) days with same latitude, e) leg 2 (14-19 March), f) leg 2 (19-22 March), g) leg 3 (26-30 March) [H.G.J. Smit, Research Centre Jülich (ICG 2), Germany].

Figure 37: 6 day back trajectories arriving at the ship at 950, 750, and 500 mbar (12Z) for DOY 53 and 54 during leg 1 (INDOEX) [http://saga.pmel.noaa.gov/indoex/traject/].
4.3.2.2.3 Satellite data

Figure 38 shows the vertical $O_3$ column of the troposphere derived by using the “excess method”. The values indicate that there is negligible transport from southern Africa into the Indian Ocean. It has to be mentioned, however, that the excess method is only reliable between 10°N and 10°S, therefore Figure 38 gives only a qualitative impression. The qualitative impression is, however, suitable to determine whether biomass burning and/or other large anthropogenic sources are present and to what extent they influence the investigated region.

Figure 39 shows the number of fires around the Indian Ocean and as expected only relatively low numbers of biomass burning activities occur during this time of the year. Figure 40 shows the lightning activities during February and March 1999. There is no indication of enhanced $O_3$ levels through local NO$_x$ production (Figure 41). Therefore, the $O_3$ present in the SH Hadley cell has been most dominantly intruded by the stratosphere, since there are no sources of $O_3$ precursors in the vicinity and the interhemispheric transport of $O_3$ remains unlikely.

In the Figure 42 and Figure 43 the vertical columns of tropospheric NO$_2$ and HCHO are presented respectively. These two trace gases reveal no new sources for $O_3$ precursors and support the observed excess tropospheric columns in Figure 38. The results by Randriambelo et al. [2000] give further evidence that during February and March there is little influence of biomass burning or other anthropogenic sources on the observed area.
Figure 38: Tropospheric O$_3$ vertical column [DU] measured by GOME (Feb./March 1999).

Figure 39: Number of fires according to Along Track Scanning Radiometer (ATSR) for Feb. and March 1999.
Figure 40: Lightning activity during Feb. and March 1999 [NASA/MSFC].
Figure 41: Lightning produced tropospheric NO$_2$ vertical columns Feb. and March 1999.
Figure 42: Tropospheric NO$_2$ vertical column measured by GOME (Feb./March 1999).

Figure 43: Tropospheric HCHO vertical column measured by GOME (Feb./March 1999).
It can be concluded that the SH \(O_3\) levels measured during the INDOEX campaign have mainly stratospheric origin. However, the influence of long range transport of \(O_3\) cannot be excluded because of the long lifetime of \(O_3\) in the middle and upper troposphere. However, the evidence for the stratospheric origin is clear. The divergence of high \(O_3\) mixing ratios in the transition zone between tropics and extratropics seems to indicate the stratospheric tropospheric exchange.

### 4.3.3 Discussion

The chemistry of the MBL over the period of the INDOEX campaign was simulated using the trace gas measurements, meteorological data, and modelling conditions described above. There is a reasonable agreement between simulated and measured trace gases on most of the days [Burkert et al., 2003a]. Analysis of the results highlights the following features.

#### 4.3.3.1 \(O_3\) depletion

The diurnal behaviour of the \(O_3\) mixing ratio within the MBL during INDOEX typically showed a daytime depletion followed by a clearly visible nocturnal recovery. The short-term variations of \(O_3\) seem to be superimposed on a latitudinal gradient, likely determined by the distance to the precursor sources.

The measured daytime \(O_3\) diurnal variations are reasonably well simulated. Note that \(O_3\) changes associated with both the latitudinal gradient and the change of air parcels (in a 24 hours period) are not considered in this simulation.

In order to rule out any interference associated to the latitudinal effect the days 72 and 73 corresponding to a horizontal transect were more closely analysed. In Figure 44 both the measured and the simulated \(O_3\) diurnal variations are plotted.
Figure 44: Diurnal variation of measured and modelled O$_3$ mixing ratios for DOY 72-73 (horizontal transect, no change in the latitude).

The considered photochemistry adequately reproduces the daytime concentrations observed. Since only daily NO averages are available, it is difficult to calculate accurately the daytime O$_3$ production term. In the case of NO being higher than the mixing ratio considered (NO$_x$ ~ 15 pptv) in the simulation, an additional loss mechanism (i.e. reactions (48), (49), and (50)) involving halogens (as suggested by Dickerson et al., [1999] and Vogt et al., [1996]) would be necessary to explain the measurements.

$$Br + O_3 \rightarrow BrO + O_2$$  \hspace{1cm} (48)

$$BrO + HO_2 \rightarrow BrOH + O_2$$  \hspace{1cm} (49)

$$BrOH + h\nu \rightarrow Br + OH$$  \hspace{1cm} (50)

Figure 45 exemplifies the relative importance of the main daytime photochemical loss reactions involved in the O$_3$ cycle of remote areas (under clear sky conditions) for both the NH (DOY 64) and SH (DOY 55).

O$_3$ photolysis is the most important contributor to O$_3$ losses and represents approximately 40% for the NH and 65% for the SH of the total. The corresponding
percentages for HO$_2$ are 20% and 10% respectively. Deposition over the surface accounts only for 5% in both hemispheres.

Figure 45 is an overview for the influence of halogens showing the possible loss of O$_3$ through reactions (48), (49), and (50) for 10 pptv BrO. According to the literature, this value can be considered as a BrO upper limit in the troposphere [e.g. Keene et al., 1990, Fan and Jacob, 1992, Finnlayson-Pitts, 1993b, Parrish et al., 1993, McKeen and Liu, 1993, Graedel and Keene, 1995, Ariya et al., 1998, Richter et al., 1998, Wagner and Platt, 1998, Vogt et al., 1996, Sander and Crutzen, 1996, Sander et al., 1997]. Under these conditions, Br contributes 25% to the total loss of O$_3$ in the NH and less than 20% in the SH.
Figure 45: Relative importance of the main first order reactions defining O₃ losses over remote areas of the MBL in the NH (a) and SH (b). The calculations have been made considering the measured amounts of j(O¹D), H₂O, OH and O₃ for DOY 73 (a) and 55 (b) respectively. The following assumptions have been made: HO₂ = ½ RO₂⁺ (i.e. RO₂+HO₂), Boundary layer height = 1000 m, deposition velocity = 0.045 cm s⁻¹ and Br = 0.05 pptv.
4.3.3.2 O\textsubscript{3} recovery

This section discusses the results of measuring nocturnal O\textsubscript{3} variation the data showing a clear recovery most days. This recovery might be the result of horizontal or vertical mixing, or a combination of both. Since the model is not accounting for any dynamic processes, recovery is not calculated by the model.

The different time of appearance of the recovery (DOY 72 at \(\sim\) 1500 hrs (UTC) and DOY 73 at \(\sim\) 2100 hrs (UTC)) suggests a time dependent effect. Two processes will be discussed explicitly, the advective process transporting O\textsubscript{3} horizontally to the observed measurement site, and the convective processes leading to an entrainment from the layer above the MBL.

4.3.3.2.1 Advective processes

It has recently been shown by de Laat [2000, 2001a, 2001b] that horizontal transport and photochemical processes can explain the typical diurnal O\textsubscript{3} cycle in the MBL close to the source region. This mechanism proposes that the daytime decrease and nighttime increase are closely related.

Daytime O\textsubscript{3} destruction, combined with horizontal advection and diffusion, creates the latitudinal gradient in O\textsubscript{3} from the source regions. This gradient causes the nighttime increase because air with higher O\textsubscript{3} concentrations is advected to regions with lower O\textsubscript{3} concentrations. Using this approach the daytime decrease will always be counteracted by the nighttime increase. The daytime depletion rate is therefore equal to the amplitude of the diurnal O\textsubscript{3} cycle. Although the horizontal advection of air masses with higher O\textsubscript{3} concentrations continues during daytime, net photochemical O\textsubscript{3} destruction dominates daytime O\textsubscript{3} behaviour.

Differences in wind speed are required in order to explain the different start-up times for O\textsubscript{3} recovery on DOY 72 and 73 by horizontal transport and the associated latitudinal gradient. This has not been observed. However, it could be argued that different air masses have been observed, but according to data of other trace gases this was not the case.

During the first leg of INDOEX SHmT air masses were observed coming from the East and with no sources available, the diurnal behaviour of O\textsubscript{3} was exactly the same. A latitudinal gradient was also observed. As the source for SH tropospheric O\textsubscript{3} during leg 1 is expected to come from the stratosphere by downward transport at the end
of the Hadley cell, the advective process would still be an excellent explanation. Also
the decrease in the latitudinal gradient in O$_3$ in the SH is in agreement with the theory.
The NH latitudinal gradient does not reveal a decrease with decreasing amount of O$_3$.
This is in disagreement with the expected behaviour.

4.3.3.2.2 Convective processes

The convective processes caused by the strong variation in the Earth’s
temperature (and the resultant vertical temperature profile) are a main source for O$_3$
transport at the surface over land [Brasseur et al., 1999, and references therein]. Over
the ocean there is only a slight T-variation.

The vertical distribution of temperature over the ocean obtained from
meteorological radiosondes, does not clearly indicate the stability of the air parcels.
According to the potential temperature the air is in almost all cases conditional unstable.
The observed lapse rate is smaller than the dry adiabatic lapse rate (on average the
gradient over ocean is between 0.6 and 0.7 °K/100 m). The virtual potential temperature
behaves similarly due to the negligible difference of the heat capacities between dry and
moisturised air. However, the effect leads only to a more stabilised atmosphere, since
the amount of water in the atmosphere has its maximum in the MBL.

For calculating the stability of an air parcel the equivalent potential temperature
(EPT) can be used as an indicator. The observed EPT indicates that the layer above the
MBL was conditionally unstable, because in the NH during INDOEX the MBL (R.H.
between 70 and 95%) was mostly covered with a dry layer (R.H. between 30 and 50%)
(Figure 46). In areas where vertical mixing is expected (i.e. ITCZ), which implies a
homogenous vertical distribution of relative humidity, the EPT indicates a conditionally
stable atmosphere. This leads to the conclusion that, either the stability of the
atmosphere is driven by other processes, or the adiabatic approach is inappropriate.
Apart from the thermodynamical view of stability two possibilities of vertical mixing have been discussed in the past, a constant entrainment [e.g. Dickerson et al., 1999], and a diurnal variable entrainment [e.g. Bremaud et al., 1998].

**Constant entrainment**

The assumption of constant entrainment can describe the nighttime recovery of ozone. However, this process seems to be unlikely because of the different recovery times for O₃ (Figure 44) and the time over which O₃ is recovered. Furthermore, this mechanism produces an additional amount of O₃ during daytime which requires another loss process to be compensated, in order to reproduce the measurements. Even halogens could not account for such an additional loss [Dickerson et al., 1999].
Diurnal variable entrainment

This section discusses the possibility of a diurnal variation of the entrainment strength. This assumption can be supported by the fact that the presence of absorbing aerosols lead to a warming of the layer where they are present.

Figure 47 shows the model results of the warming rate (K h\(^{-1}\)) due to the absorption of direct solar radiation by aerosols derived from PHOTOST for an AOD of 0.47 and a vertical distribution as measured by Welton et al. [2002]. According to the observed air masses in the NH especially the NHcT and NHcX regimes, there was always a highly polluted aerosol layer above the MBL [Welton et al., 2002]. The described effect leads to an entrainment velocity which is dependent on the solar radiation and the amount of absorbing aerosols. The warming over a day is about 1°K in the aerosol layer (~1 to 3 km) which is significant compared to a dry adiabatic lapse rate. However, there was no systematic difference in the extension of the temperature inversions observed [radiosonde data, http://saga.pmel.noaa.gov/indoex/index.html], that would indicate a change in the entrainment strength between day and night. The only evidence for the warming effect of aerosols can be seen in Figure 49, where the temperature profiles from sondes have been averaged according to the air mass characterisation by Welton et al. [2002] shown in Figure 48.

These averaged vertical temperature profiles show an increasing slight inversion layer (i.e. the vertical temperature gradient decreases to ~0°K/m) as the air masses change the cleaner (C1-C3) to the more polluted regions (C4-C6). The change from the cleaner region to the more polluted region coincidences with an enhancement in the amount of absorbing aerosols [Dickerson et al., 2002].
Figure 47: Modelled warming rates caused by aerosols for different AOD at a SZA of 30°. Composition and vertical distribution are described in Table 5 and Figure 23 respectively.

Figure 48: Air mass trajectories at 0.5, 2.5, and 5.5 km are shown for each category defined in the text. The C1, C2, C3, C5, and C6 trajectory patterns are shown in (a), and C4 trajectory patterns are shown in (b) [Welton et al., 2002].
The O$_3$ (2km)/O$_3$ (0km) ratio gives some information about the entrainment strength from the layer above into the MBL. Table 3 presents the daily averaged O$_3$ mixing ratios in the MBL [Stehr et al., 2002] and at 2km height [Figure 9] measured on board the RV Ron Brown. On most of the days the ratio is about 1.6 +/- 0.5, which indicates that the possible variability in the entrainment strength is not high. The correlation between AOD and the ratio is well pronounced (Figure 22) and supports the effect of aerosols and radiation on the vertical temperature structure.

Despite this, on DOY 85 and 86 the O$_3$ (at 2 km)/ O$_3$ (at 0 km) ratio was above 5 while the diurnal cycle of O$_3$ showed a decreasing O$_3$ mixing ratio during the day and a recovery after sunset to the same level as before sunrise. Taking into account that the O$_3$ mixing ratio in the MBL was ~15 ppbv and the mixing ratio at 2 km height was ~71 ppbv, the two layers seem to be isolated from each other. The AOD during these two
days was around 0.4, which is comparable to the AOD measured in the NHcT and NHcX regimes.

<table>
<thead>
<tr>
<th>DOY</th>
<th>$O_3$ (2km) [ppbv]</th>
<th>$O_3$ (0 km) [ppbv]</th>
<th>$O_3$(2km)/$O_3$(0km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>22</td>
<td>11</td>
<td>2</td>
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<tr>
<td>56</td>
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<td>1.3</td>
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<tr>
<td>88</td>
<td>25</td>
<td>20</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 3: Daily $O_3$ mixing ratio at ground level and at 2 km and the resultant ratio.
Overall, it seems to be impossible with the information presented here to rule out any of the above mentioned processes. The possibility of a diurnal variation in the entrainment strength seems to be most likely, although accepting this process still includes the presence of other possible loss processes (such as halogens) for explaining the diurnal behaviour of O3.

In addition, diurnal variation in the entrainment strength still includes entrainment during the day, however it only gives evidence for less daytime entrainment than nighttime entrainment.

### 4.3.4 Interpretation

The measurements of vertical O3 profiles in the SH, together with satellite pictures of a variety of trace gases have shown in a qualitative way the strong influence of stratospheric O3 within the troposphere. The satellite pictures show that the influence of biomass burning or lightning produced NOx in the area of observation was minimal.

Other possible sources of O3 and its precursors are far away, but due to the long lifetime of O3 in the middle and upper troposphere this influence cannot be neglected.
However, taking all the data into account it appears that the amount of STE of O$_3$ was the major source in the SH Indian Ocean during February and March.

Overall, the collected data give the excellent opportunity to analyse the reliability of global models in this area. Therefore, a comparison of the data with model results should be performed in the future.

A zero dimensional model was used to investigate the diurnal evolution of O$_3$ concentrations. The known chemistry without any entrainment or horizontal transport and without halogens can describe the daytime decrease of O$_3$. The role of halogens, however, must be reconsidered when transport processes are leading to an additional source in the model. The expected bromine concentrations can account for about 20% of the total O$_3$ loss [Dickerson et al., 1999].

The qualitative analysis of the two dynamical processes most likely responsible for the nocturnal recovery of O$_3$ revealed that neither of them alone can explain the observed behaviour. As a result of this work, convective processes will have to be reconsidered in all models concerning the influence of aerosols. For example, the encountered aerosols during INDOEX can lead to warming rates in the free troposphere of about 1°K a day (AOD of 0.6 and an aerosol composition as described above) which is sufficient to stabilise the atmosphere.

The analysis has shown that neither the convective nor the advective processes on their own can explain the observed diurnal behaviour of O$_3$. A combination of both processes appears reasonable, but a more detailed analysis of the micro and macro meteorological parameters is required.

It can be summarized that the daytime destruction of O$_3$ is well reproduced by the known chemistry, but the presence of for example halogens cannot be ruled out and absorbing aerosol can be responsible for a diurnal variation in the entrainment strength. In future studies of this type it is suggested that this information should be collected so that it can improve chemical knowledge in the MBL.
5 PRIME campaign

5.1 Introduction

The Institute of Environmental Physics of the University of Bremen (IUP-UB) and the University of Leeds (Uni-Leeds) participated in a EU project called PRIME (Peroxy Radical Initiative for Measurements in the Environment). It consisted of a field campaign to measure tropospheric trace gases near London during the period July-August 1999.

One of the objectives of the field work was to investigate the role of oxy-, hydroxy-, and peroxy radicals in urban environments, and to characterise sources and sinks of these radicals in the troposphere. Therefore an extensive suite of ancillary measurements necessary for photochemical modelling, including measuring levels of trace gases, photodissociation rates and meteorological parameters, also formed part of the study (see http://www.huxley.ic.ac.uk/research/emma/prime/).

In the present study, measurements of RO$_2^*$, NO, NO$_2$, PAN, and CO performed by the IUP-UB and H$_2$O$_2$ and ROOH made by the Uni-Leeds are presented and compared with the results from a zero dimensional model. The discussion focuses on the measured daytime amounts of RO$_2^*$ in relation to HO$_2$ using the FAGE technique (Fluorescence Assay with Gas Expansion) [Creasey et al., 1997, Carslaw et al., 1999], and to the peroxide measurements of the Uni-Leeds. In addition, one issue of special interest is the coexistence of high amounts of NO and RO$_2^*$, especially in the early morning hours.
5.2 Results and discussion

5.2.1 Air mass classification and measurement site description

According to the back trajectories [British Atmospheric Data Centre – Trajectory service, http://www.badc.rl.ac.uk/], three different types of air masses (hereafter referred to as North West, East and South-West) were identified during the course of this study at the measuring site.

Figure 50 represents typical back trajectories for the different air masses. In the case of North-West trajectories the air parcels originated from south of Iceland and passed the northern part of the UK before reaching London. The eastern air mass initially came from the north and north east. The air passes the European Continent before heading towards London. Locally these air parcels reached the measurement site from the East and South East. The south-west air masses originated over the Atlantic Ocean, passing over the north western part of Spain and the north western part of France reaching London from the South-West.

Three classes have been identified as being significantly different in terms of air mass origin and composition, whereas the latter is superimposed by local emissions. The types of air masses (North-West, East, and South-West) comprise the following periods:

- North-West: 23.7 – 27.7; 10.8 –12.8
- East: 28.7 – 3.8; 9.8
- South-West: 4.8 – 8.8

As the local wind direction is independent of the air mass origin, the origin of the air mass is only relevant for long lived species not emitted by local sources.
Figure 50: Typical 5-day back trajectories for a) North-West (23.7 – 27.7; 10.8 – 12.8), b) East (28.7 – 3.8; 9.8), c) South-West (4.8 – 8.8) [British Atmospheric Data Centre – Trajectory service, http://www.badc.rl.ac.uk/].
The measurement site, although located in a park, is surrounded by roads with significant traffic. In general, the diurnal behaviour of the trace gases in the area of study is expected to be mainly determined by the local/regional emissions. During the period field measurements were taken local winds were of variable intensity, indicating an unsteady influence of local emissions in the air composition measured. Therefore, and as a consequence of the rough resolution of the trajectories, no clear correlations between trace gases and general air flows are expected.

Two episodes of elevated concentrations of trace gases were observed, from the 23rd to the 25th July, by North-West conditions and from the 29th July to the 3rd August, characterised by East trajectories. Jenkin et al. [2000b] have recently reported that the most intense photochemical ozone episodes are associated with trajectories over mainland Europe where they are enriched with VOC and NOx for several days before arriving in the UK from a broadly eastern or south-eastern direction.

5.2.2 Trace gas measurements

In the following the complete dataset recorded during the PRIME campaign by the IUP-UB and the Uni-Leeds is presented. The NO, NO2, CO, RO2*, and PAN mixing ratios measured by the IUP-UB are shown in Figure 51. The O3 mixing ratios measured by Imperial College are also included for clarification. The different air masses are labelled on top of the figures.
Figure 51: RO2*, CO, O3, NO, NO2, and PAN mixing ratios measured during the PRIME 1999 field campaign.
Figure 51: RO$_2^*$, CO, O$_3$, NO, NO$_2$, and PAN mixing ratios measured during the PRIME 1999 field campaign.
Figure 51: $\mathrm{RO}_2^*$, $\mathrm{CO}$, $\mathrm{O}_3$, $\mathrm{NO}$, $\mathrm{NO}_2$, and PAN mixing ratios measured during the PRIME 1999 field campaign.
Two periods have been identified as being highly photochemical active: 23\textsuperscript{rd}-26\textsuperscript{th} July and 29\textsuperscript{th}-3\textsuperscript{rd} August. The other periods are characterised by lesser amounts of all reactive trace species. Figure 52 shows the measured amounts of HO\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}, and CH\textsubscript{3}OOH by the Uni-Leeds.
Figure 52: HO$_2$ (x 100), H$_2$O$_2$, and CH$_3$OOH mixing ratios measured during the PRIME 1999 field campaign.
5.2.2.1 General diurnal behaviour of trace gases

Over the general long term evolution of the air composition, some diurnal features are observed at the measurement site.

NO\textsubscript{2} mixing ratios increase typically at dawn as a result of the NO\textsubscript{x} local emissions (i.e. for example rush hour) followed by the subsequent titration of O\textsubscript{3} with NO and the low radiation (i.e. low photolytical decompositon of NO\textsubscript{2}). This effect is enhanced by the build up of the nocturnal planetary boundary layer (PBL) during the night, which captures the emission within a much smaller volume compared to the daytime PBL. This is corroborated by the CO nocturnal increase which mostly correlates temporally with the NO\textsubscript{2} variation.

The NO\textsubscript{2} maximum is reached before sunrise. Afterwards, high amounts of NO\textsubscript{2} are produced as it becomes photodissociated to form NO and O\textsubscript{3}. This effect, together with the morning rush hour vehicle traffic leads to a maximum in the NO mixing ratio and a maximum in the O\textsubscript{3} production (d[O\textsubscript{3}]/dt).

With increasing solar radiation the nocturnal PBL vanishes favouring entrainment from above and mixing. Therefore, the direct emissions are diluted, which prevents a further increase in the NO\textsubscript{x} mixing ratio. The well mixed PBL around noon is characterised by production of O\textsubscript{3} via the reaction of RO\textsubscript{2}\textsuperscript{*} with NO and the subsequent photodissociation of NO\textsubscript{2}. As expected, PAN and O\textsubscript{3} present a very similar diurnal evolution reaching maximum mixing ratios in the late afternoon. However the O\textsubscript{3} plateau generally persists longer than in the case of PAN.

The diurnal behaviour of the RO\textsubscript{2}\textsuperscript{*} concentration is explained in more detail in the next section. It is typically characterised by an increase after the NO maximum, reaching a maximum around noon and staying at a constant level till afternoon. During sunset the RO\textsubscript{2}\textsuperscript{*} concentration decreases and remains at a nocturnal value which likely depends on the amount of NO\textsubscript{3} and O\textsubscript{3} available.

The HO\textsubscript{2} mixing ratios seem to support the presence of non negligible amounts of radicals in the evening. During the day the behaviour is comparable to the behaviour of the RO\textsubscript{2}\textsuperscript{*}, with a stronger decrease in the afternoon due to the faster loss reactions of HO\textsubscript{2} compared to RO\textsubscript{2}.

The CH\textsubscript{3}OOH diurnal profile is variable, the data shown here does not reveal a clear daily cycle. By contrast, the mixing ratios of H\textsubscript{2}O\textsubscript{2} increase at sunrise reaching their maximum during midday, remaining at that level until late afternoon (Figure 52).
Taking into account that H$_2$O$_2$ is exclusively produced via the HO$_2$ self reaction and that production dominates over losses during the day, a correlation of the daily maxima of HO$_2$ and H$_2$O$_2$ is expected, but is not observed.

### 5.2.2.2 Peroxy radical diurnal variation

The measured RO$_2^*$ diurnal behaviour reflects the photochemical nature of these radicals. The increase in the mixing ratios with increasing solar radiation in the morning is retarded by the presence of NO. The maximum level was generally reached around noon and varied between 15 and 70 pptv during the campaign. After 3-4 hours at an almost constant level of concentration, the RO$_2^*$ mixing ratios decreased to a minimum.

The most striking feature of the PRIME radical dataset is the detection of significant amounts of RO$_2^*$ in the presence of high NO concentrations (Figure 2). This situation is observed repeatedly in the period of high mixing related to the increase of the PBL height at around 9-10 am. The observed coexistence of NO and RO$_2^*$ cannot be explained easily if the time scale of mixing and chemistry are of similar magnitude. The chemistry is expected to be dominated by the reactions of NO with RO$_2^*$ ((86)-(87)), leading to a RO$_2^*$ lifetime of about 1-2 seconds for 3-5 ppb NO.

First of all it is important to rule out a measurement error as an explanation for this RO$_2^*$ in the presence of high NO concentrations anomaly. The complexity and variability of the trace gas composition complicates the measurement of radicals in polluted areas. Very fast variations (within the minute range of the measurements) in the O$_3$ and NO$_2$ ambient levels which constitute the background signal of the PERCA can result in an artificial signal, which if not adequately corrected can lead to a wrong interpretation. The IUP-UB considers this effect by switching every 30 seconds between background and signal mode and averaging the background signal before and behind the signal mode. Therefore, the expected error is small and should be negligible while averaging the 1 minute values over longer time intervals.

The 31$^{st}$ of July (Figure 53) is selected as representative of days with active photochemistry at the measurement site. This is one of the days measured during the second episode of elevated concentrations during the PRIME campaign. The analysis concentrates on the variations produced by the model as a function of the assumed amounts of hydrocarbons and CO. The model results represent a sensitivity study focused on the chemistry of HO$_2$, RO$_2$, OH, and the peroxides. Both the ratio between
HO$_2$ and RO$_2$ and the total amount of radicals present will be discussed, especially in the case of high NO concentrations in the morning hours (see shaded area in Figure 53).

![Graph showing NO, NO$_2$, RO$_2^*$, HO$_2$ x 6, O$_3$, and OH x 1000 mixing ratios on the 31st of July between 600 and 1800 (UTC) during the PRIME campaign.](image)

Figure 53: NO, NO$_2$, RO$_2^*$, HO$_2$ x 6, O$_3$, and OH x 1000 mixing ratios on the 31st of July between 600 and 1800 (UTC) during the PRIME campaign.

### 5.2.2.3 Nocturnal radical mixing ratios

The model used here does not consider heterogeneous chemistry, a factor which has a significant impact, particularly on the amount of NO$_3$ present. Therefore this section should be treated as an outlook for further modelling perspectives and measurement campaigns.

On several days the nocturnal RO$_2^*$ mixing ratio showed significant amounts above the detection limit. Nocturnal RO$_2^*$ mixing ratios have been measured before [Cantrell et al., 1992, Hu and Stedman, 1995, Mihelcic et al., 1993, Burkert et al., 2001a, 2001b, 2003a and 2003c]. Bey et al. [2001a, and 2001b] have studied the radical nighttime tropospheric chemistry of different scenarios and found that the peroxy radical concentrations peak at night at 40 pptv in the urban case with OH concentrations ranging from 1 to 6x10$^6$ molecules cm$^{-3}$. 
The production of OH is attributed to ozonolysis of alkenes or to the conversion of peroxy radicals initially formed by VOC+NO$_3$ or VOC+O$_3$ reactions. In an urban scenario under nocturnal NO mixing ratios on the range of our measurements (100-200 pptv), the NO$_3$ radical seems to play only a secondary role both in the formation of RO$_2$, which are produced directly by ozonolysis of alkenes or indirectly from the reactions of the OH produced and other VOC, and in the production of HO$_2$, which mainly occurs via conversion RO$_2$ to HO$_2$ by RO$_2$ + NO reactions.

Increasing the content of biogenic VOC, like isoprene and terpenes, can however increase notably the importance of the contribution of the NO$_3$ reaction path to the primary production of RO$_2$ radicals. However the participation of NO$_3$ to the recycling of radicals remains negligible relative to NO [Bey et al., 2001b].

During the PRIME campaign the average isoprene mixing ratios were usually between 100 and 300 pptv. Interestingly the higher isoprene mixing ratios were coincided with pollution episodes because of the sunny conditions and higher temperatures associated to the smog episodes observed during PRIME.

Significant nocturnal RO$_2^*$ mixing ratios were observed on the 24$^{th}$, 29$^{th}$, 30$^{th}$ and 31$^{st}$ of July and on August the 1$^{st}$. The discussion of the nocturnal behaviour of RO$_2$ and HO$_2$ will be subject of a paper published separately [Burkert et al., 2003d].

### 5.2.3 Model results

This section compares model results and measurements, starting with a base case. In this base case the simulations were performed while constraining the model to the actual measurements of CH$_4$, CO, NO, NO$_2$, and propene and ethene equivalent calculated according to reactions (144) and (145) on July 31$^{st}$. The propene and ethene equivalent considers the C$_3$-C$_6$ NMHC measurements by University of Leeds.

$$[\text{propene equivalent}] = \sum [\text{alkene}] \left( \frac{n^\circ C_{\text{alkene}}}{3} \right) \left( \frac{k_{\text{OH-alkene}}}{k_{\text{OH-C}_3H_6}} \right)$$  \hspace{1cm} (144)

$$[\text{ethane equivalent}] = \sum [\text{alkane}] \left( \frac{n^\circ C_{\text{alkane}}}{2} \right) \left( \frac{k_{\text{OH-alkane}}}{k_{\text{OH-C}_2H_6}} \right)$$  \hspace{1cm} (145)

The assumed amounts for the NMHC in the model are expected to be a lower limit, because the propene equivalent is calculated only for the measured species, and
Chapter 5: PRIME campaign

According to Lewis et al., [2000] the measured amounts of the C₃-C₆ NMHC represent only approximately 30% of the total. Therefore, all unmeasured species, if present, should increase the values used. However, in order to account for this effect each of the NMHC was varied over a large range of mixing ratios (Figure 54). This should be sufficient to cover the unmeasured real case for the interpretation of the possible amounts and ratios of RO₂ and HO₂ in urban environments.

![Diagram](https://via.placeholder.com/150)

Figure 54: Overview of the different cases considered in the sensitivity study.

### 5.2.3.1 Base case

In the base case the following trace gas mixing ratios have been assumed: [CO]=400 ppbv, [CH₄]=4 ppmv, [C₂H₄]=4 ppbv, [C₂H₆]=800 ppbv, [C₃H₆]=8500 pptv. The modelled and measured amounts of HO₂, RO₂ *, NO and O₃ are shown in Figure 55.

There is a good agreement between RO₂ * measured and modelled values whereas the amounts of HO₂ differ quite substantially. However, in the early morning hours both the measured HO₂ and RO₂ * amounts are significantly higher than the resulting amounts from the model. This is most likely caused by the presence of high amounts of NO especially in the early morning hours (Figure 53 and Figure 55).
Figure 55: Modelled (dotted lines) and measured (solid line) HO$_2$ and RO$_2$* mixing ratios for the 31$^{st}$ of July 1999 during the PRIME campaign.
The NO reactions involved in the radical interconversion dominate over the other reactions. Assuming the steady state the following equations result.

\[
\frac{d[RO_2]}{dt} = -k_{NO,RO_2}[NO][RO_2] + k_{OH,HC}[OH][RH] + k_{Cl,Alkanes}[Cl][Alkanes] \\
+ k_{NO,H}[NO][RH] - k_{RO_2,HO_2}[RO_2][HO_2] \pm ...
\]

(146)

\[
\frac{d[HO_2]}{dt} = -k_{NO,HO_2}[NO][HO_2] + k_{OH,CO}[OH][CO] + k_{CH,O,CH_3}[CH_3O][O_2] \pm ...
\]

(147)

\[
\frac{d[OH]}{dt} = k_{NO,HO_2}[NO][HO_2] - k_{OH,RH}[OH][RH] - k_{OH,CO}[OH][CO] \\
+ k_{O(D),H,O}[O(1D)][H_2O] + 2 \cdot j_{H,O}[H_2O] \pm ...
\]

(148)

\[
[OH] = \frac{k_{NO,HO_2}[NO][HO_2] + k_{O(D),H,O}[O(1D)][H_2O] + 2 \cdot j_{H,O}[H_2O之外]}{k_{OH,RH}[RH] + k_{OH,CO}[CO] + ...}
\]

(149)

\[
[RO_2] = \frac{k_{OH,RO_2}[OH][RH] + k_{Cl,Alkanes}[Cl][Alkanes] + k_{NO,H}[NO][RH] + ...}{k_{NO,RO_2}[NO] + k_{RO_2,HO_2}[RO_2] + ...}
\]

(150)

These strongly simplified steady state approaches (equations (146)-(148)) illustrate the close interdependence between \( RO_2 \), \( HO_2 \), and \( OH \) caused by their chain reaction involving NO, CO, and HC. The equations (149) and (150) show that the \( OH \) and \( RO_2^* \) quantities respond non linear to the variation of hydrocarbons. Nevertheless, this interdependence can be clarified by considering only the dominant reactions of (149) and (150) (in black). For example, doubling the hydrocarbon mixing ratio leads to a doubling and a halving of the \( RO_2^* \) and \( OH \) mixing ratio, respectively.

The mixing ratio of neither of these species does therefore effectively change because \( OH \) and hydrocarbons are involved in both equations (149) and (150). The dominance of the NO reactions over the reactions marked in grey leads to the conclusion that in the presence of sufficient high NO mixing ratios, the \( OH \), \( RO_2 \), and \( HO_2 \) amounts are mainly controlled by NO.

As can be seen in Figure 55, while the \( RO_2^* \) diurnal evolution is reasonably well reproduced, the \( HO_2 \) mixing ratios are clearly overestimated by the model. Therefore, the ratio between \( RO_2^* \) and \( HO_2 \) is highly underestimated. The possible variability of this ratio will be investigated in sections 5.2.3.2 - 5.2.3.7.
5.2.3.2 CO variation

Figure 56 shows the base (case) and four additional cases corresponding to 0 ppbv, 4 ppbv, 40 ppbv, and 4 ppmv CO.

a)

![Graph showing diurnal variation of HO2 model for CO concentrations.]

b)

![Graph showing diurnal variation of RO2* model for CO concentrations.]

Figure 56: Diurnal variation of modelled HO2 and RO2* mixing ratio for CO 0 ppbv, 4 ppbv, 40 ppbv, base case (400 ppbv), and 4 ppmv.
Even a variation of the CO mixing ratio (Figure 56) up to 4 ppmv leads to an increase in the amount of peroxy radicals of less than 20%. Therefore, the amount of peroxy radicals in the area of observation seems to be determined by the amount of hydrocarbons present. The difference between the corresponding ratios of RO₂* and HO₂ is small and close to constant as a consequence of the high amounts of NO present. The NO converts very rapidly the RO₂ into HO₂ and a change in the amount of CO has little impact on the amounts of HO₂.

5.2.3.3 CH₄ variation

Figure 57 shows the diurnal variations of HO₂ and RO₂* for different CH₄ (0 ppbv, 400 ppbv, 4 ppmv, 40 ppmv) mixing ratios. As in the case of the CO variation, the HO₂ concentration remains invariable except for the “unrealistic” 40 ppmv case. The same is true for the RO₂* mixing ratios.
Figure 57: Diurnal variation of modelled HO$_2$ and RO$_2^*$ mixing ratios for CH$_4$ 0 ppbv, 400 ppbv, base case (4 ppmv), and 40 ppmv.
5.2.3.4 \textbf{C}_2\text{H}_4 \textbf{variation}

Figure 58 shows the diurnal variation of HO$_2$ and RO$_2^*$ for C$_2$H$_4$ 0 pptv, 400 pptv, 4 ppbv (base case), 40 ppbv, and 400 ppbv. As in the former cases HO$_2$ does not vary except for the 40 ppbv and 400 ppbv case. The same is observed for the RO$_2^*$ mixing ratios.

The influence of the C$_2$H$_4$ concentrations on the amount of peroxy radicals up to 4 ppbv C$_2$H$_4$ is negligible. The shape of the diurnal profile of both the HO$_2$ and RO$_2^*$ mixing ratio seems not to change significantly up to C$_2$H$_4$ levels of 40 ppbv. The 400 ppbv C$_2$H$_4$ case, however, has a different shape. The shape seems to follow the solar radiance, as expected.

At these high levels of C$_2$H$_4$ the early morning production of OH is predominantly defined by the amounts of C$_2$H$_4$ present. Therefore, in agreement with the model results, the OH diurnal profile adopts the form shown in Figure 58 for HO$_2$ and RO$_2^*$. The influence of NO seems to have become negligible.

Although these high values are unrealistic, they illustrate the behaviour of atmospheric trace gases by turning from a regime dominated by the NO$_x$ present to a regime dominated by the C$_2$H$_4$. 
Figure 58: Diurnal variation of modelled HO\textsubscript{2} and RO\textsubscript{2}* mixing ratio for C\textsubscript{2}H\textsubscript{4} 0 pptv, 400 pptv, 4 ppbv (base case), 40 ppbv, and 400 ppbv.
5.2.3.5 $\text{C}_2\text{H}_6$ variation

Figure 59 shows the diurnal variation of HO$_2$ and RO$_2^*$ for different $\text{C}_2\text{H}_6$ (0 ppbv, 8 ppbv, 80 ppbv, 800 ppbv (base case), 8 ppmv, 80 ppmv) mixing ratios. The amounts of HO$_2$ show no significant increase up to 8 ppmv of $\text{C}_2\text{H}_6$.

In Figure 59 b) the RO$_2^*$ mixing ratios seem not to be influenced by the variation of $\text{C}_2\text{H}_6$, up to 800 ppbv.

Overall it can be summarised that the impact of $\text{C}_2\text{H}_6$ on the amount of peroxy radicals is small and comparable to the influence of $\text{CH}_4$ and CO. In addition, increasing amounts of $\text{C}_2\text{H}_6$ change the ratio between RO$_2$ and HO$_2$ towards more RO$_2$. 

Figure 59: Diurnal variation of modelled HO$_2$ and RO$_2^*$ mixing ratio for C$_2$H$_6$ 0 ppbv, 8 ppbv, 80 ppbv, 800 ppbv (base case), 8 ppmv, and 80 ppmv.
5.2.3.6 $\text{C}_3\text{H}_6$ variation

Figure 60 shows the diurnal variation of HO$_2$ and RO$_2^*$ for different $\text{C}_3\text{H}_6$ (0 pptv, 85 pptv, 850 pptv, 8500 pptv (base case), and 85 ppbv) mixing ratios. The variation of $\text{C}_3\text{H}_6$ mixing ratios have a much higher influence on the amounts of RO$_2^*$ and HO$_2$ than all previous cases, due to the higher amounts of radicals produced through each step of oxidation. Again a transition is observed in the diurnal shape, starting from a highly structured diurnal profile (the result of the variation of NO) and moving into a more smooth profile correlated with solar radiation.
Figure 60: Diurnal variation of modelled HO\textsubscript{2} and RO\textsubscript{2}* mixing ratio for C\textsubscript{3}H\textsubscript{6} 0 pptv, 15 pptv, 150 pptv, 1500 pptv, 15 ppbv (base case), 150 ppbv, and 1500 ppbv.
5.2.3.7 \( \text{C}_3\text{H}_6 \) variation with 10 times higher reactivity with \( \text{O}_3 \)

Figure 61 shows the diurnal variation of \( \text{HO}_2 \) and \( \text{RO}_2^* \) for different amounts of \( \text{C}_3\text{H}_6 \) (0 pptv, 85 pptv, 850 pptv, 8500 pptv (base case), and 85 ppbv). In this case study the reaction of \( \text{O}_3 \) with \( \text{C}_3\text{H}_6 \) was enhanced by a factor of 10. We also enhanced the reaction rate coefficient to estimate how the behaviour of peroxy radicals change if species like diene (especially: terpene) are present.

To a good approximation the dienes react on average ten times faster than the mono-alkenes. In comparison with Figure 60 the mixing ratio of the peroxy radicals in Figure 61 are slightly higher. Focussing on the maximum daytime mixing ratios the increase between case 5.2.3.6 and 5.2.3.7 is below 20% for \( \text{C}_3\text{H}_6 \) mixing ratios below 850 pptv and increase to differences of more than 50% for maximum \( \text{RO}_2^* \) for the base case (8500 pptv). Interestingly, the ratio between \( \text{RO}_2^* \) and \( \text{HO}_2 \) is not changing within the simulated range of \( \text{C}_3\text{H}_6 \) mixing ratios. Therefore, we conclude that the amount of NO present defines the ratio between \( \text{HO}_2 \) and \( \text{RO}_2^* \).

The enhancement in the \( \text{O}_3 \) and \( \text{C}_3\text{H}_6 \) reactions leads to a strong increase in the amount of all radicals (i.e. \( \text{OH} + \text{RO}_2^* \)) present, but this increase is not caused by the direct production of peroxy radicals, but it is rather caused by an increase in the total amount of all radicals.
Figure 61: Diurnal variation of modelled HO$_2$ and RO$_2^*$ mixing ratio for C$_3$H$_6$ 0 pptv, 15 pptv, 150 pptv, 1500 pptv, 15 ppbv (base case), 150 ppbv, and 1500 ppbv (the O$_3$ with C$_3$H$_6$ reaction rate coefficient is enhanced by a factor of 10).
5.2.3.8 \( \text{RO}_2^* \) to \( \text{HO}_2 \) ratio

Sections 5.2.3.1 to 5.2.3.7 have shown that the maximum \( \text{RO}_2^* \) and \( \text{HO}_2 \) mixing ratios vary only slightly. Therefore, the ratio between max \( \text{RO}_2^* \) and max \( \text{HO}_2 \) under heavily polluted conditions is expected to be constant. The steady ratio seems to be caused by the fast reactions with NO dominating the loss and/or interconversion of peroxy radicals leading to lifetimes of a few seconds (see section 5.2.3.1).

Consequently, the ratio between max \( \text{RO}_2^* \) and max \( \text{HO}_2 \) is insensitive to the amount of precursors present. The ratio of the maximum daytime \( \text{RO}_2^* \) and \( \text{HO}_2 \) mixing ratios varies in all studied cases between 1.1 and 2.3. Neglecting the cases in which the base case concentrations have been enhanced or reduced by two orders of magnitude or more the resultant ratios vary only between 1.4 and 1.7.

5.2.4 Comparison between model and measurements

This chapter will focus on the comparison between the modelled and measured \( \text{RO}_2^* \) to \( \text{HO}_2 \) ratio and the amounts of \( \text{H}_2\text{O}_2 \) and \( \text{OH} \).

5.2.4.1 \( \text{RO}_2^* \) to \( \text{HO}_2 \) ratio

The measured ratio between maximum \( \text{RO}_2^* \) and \( \text{HO}_2 \) is significantly higher than that expected based on the results of the sensitivity study presented in chapter 5.2.3 (Table 7). In general the ratio was between 7 and 10, the deviating values corresponding to cloudy days, when the radiation reaching the ground was substantially reduced.
### Table 7: Measured daily average and maximum mixing ratios for OH, HO\(_2\), and RO\(_2^*\) during the PRIME campaign 1999.

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<td>0.069</td>
<td>0.155</td>
<td>3.6</td>
<td>9.3</td>
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<td>24. Jul</td>
<td>0.091</td>
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<tr>
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<tr>
<td>26. Jul</td>
<td>0.095</td>
<td>0.214</td>
<td></td>
<td></td>
<td>5</td>
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<tr>
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<td>0.157</td>
<td>2.8</td>
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<td>6.8</td>
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<td>2. Aug</td>
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<tr>
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<tr>
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<td>0.128</td>
<td></td>
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</tbody>
</table>

Comparing the measured RO\(_2^*\) to HO\(_2\) ratios (7-10) with the modelled ratios (1.3-2) it becomes obvious that there is a large gap between the actual observations and theory. As will be discussed later the RO\(_2^*\) levels measured within PRIME are in agreement with other studies in similar areas, when the measurements are corrected for the water interference of the PERCA [Burkert et al., 2001b, Reichert et al., 2003].

### 5.2.4.2 H\(_2\)O\(_2\) mixing ratio

It is important to note that at these observed low levels of HO\(_2\) the modelled H\(_2\)O\(_2\) clearly underestimates the measurements. As H\(_2\)O\(_2\) is expected to be formed exclusively from the HO\(_2\) self reaction this underestimation indicates an inconsistency in the chemistry or in the measurements considered, and/or discrepancies among the species involved in the interconversion of OH and peroxy radicals.
One possible explanation is that \( H_2O_2 \) is not exclusively produced via the \( HO_2 \) self reaction. Several studies in the literature [Horie et al., 1994, Gäb et al., 1995, Neeb et al., 1997, Wolff et al., 1997, Sauer et al., 1999] discuss the possibility of the production of \( H_2O_2 \) through the ozonolysis of alkenes and the subsequent reaction.

\[
CH_2 = CHR + O_3 \rightarrow \text{primary ozonide} \quad (117)
\]

\[
\text{primary ozonide} \rightarrow CH_2OO^+ + RCHO \quad (118)
\]

\[
CH_2OO^+ + M \rightarrow CH_2OO + M \quad (119)
\]

\[
CH_2OO + H_2O \rightarrow CH_2O + H_2O_2 \quad (120)
\]

\( R \) represents the organic group and corresponds to \( H \) in the case of ethene. These reactions (117) to (120) are not the dominant pathways, however, they can contribute significantly to the total amount of \( H_2O_2 \).

Figure 62 shows the contribution of reaction (120) to the total amount of \( HO_2 \) present, simulated for the base case. This simulation used a rate constant of \( k=6\times10^{-18} \) (molec cm\(^{-3}\)) as assumed in the MCM2 model [http://chmlin9.leeds.ac.uk/MCMframe.html].

Recent literature contains controversial discussion, about whether the production of \( H_2O_2 \) via this reaction path takes place at all [Geert Moortgat, personal communication, 2002]. Neeb et al. [1997] observed no significant production of \( H_2O_2 \) and found that formation of HCHO was linearly coupled to the consumption of alkenes, indicating that HCHO is formed only as a primary product from the primary ozonide [Hatakeyama and Akimoto, 1994] (see section 2.2.2.4).
Figure 62: Diurnal variation of $\text{H}_2\text{O}_2$ mixing ratios of the base case, the observations, and the base case with additional production of $\text{H}_2\text{O}_2$ via reaction (120).

Interesting to note is the earlier production of $\text{H}_2\text{O}_2$ in Figure 62 for the case of “additional production via reaction (120)”.

However, as the model cannot describe the early morning radical behaviour, the beginning of the modelled $\text{H}_2\text{O}_2$ production is delayed. If the amount of radicals in the early morning were adequately simulated another production process for $\text{H}_2\text{O}_2$ besides the HO$_2$ self reaction would not be necessary. Figure 62 shows the corresponding $\text{H}_2\text{O}_2$ amount modelled assuming that half of the RO$_2^*$ measured is HO$_2$.

In Figure 63 the $\text{H}_2\text{O}_2$ mixing ratios which correspond with the maximum amounts of HO$_2$ are shown to reveal the inconsistency between the measured HO$_2$ (up to 10 pptv) and the measured $\text{H}_2\text{O}_2$ (up to 1000 pptv). A simulated HO$_2$ diurnal profile reaching a maximum of 10 pptv corresponds with a $\text{H}_2\text{O}_2$ diurnal maximum of no more than 50 pptv.

In addition, as can be seen in Figure 55, the base case simulation can reproduce the measured RO$_2^*$ mixing ratios. The corresponding maximum daytime mixing ratios of HO$_2$ and $\text{H}_2\text{O}_2$ are approximately 38 pptv and 1200 pptv, respectively, therefore the amount of $\text{H}_2\text{O}_2$ in the base case is in the range of the observations.
Finally, it can be concluded that either a reaction which produces high amounts of \( \text{H}_2\text{O}_2 \) is missing or there is an artefact in the measurements of either \( \text{HO}_2 \) or \( \text{H}_2\text{O}_2 \).

Figure 63: Diurnal profiles of measured and simulated amounts of \( \text{H}_2\text{O}_2 \) for different \( \text{HO}_2 \) mixing ratios.

### 5.2.4.3 OH mixing ratio

The increase in the total amount of available radicals and therefore in the amount of available OH radicals leads to the highest amounts of peroxy radicals, as can be seen in the diurnal profile of the radicals.

Figure 64 shows that the model can reproduce the measured OH mixing ratios. However, the OH diurnal profile shows a late afternoon peak which cannot be described by the model. Even the assumption that all present \( \text{C}_3\text{H}_6 \) are reacting 10 times faster with \( \text{O}_3 \) than described in the literature (i.e. we assume that all alkenes are dienes (especially terpenes)) does not lead to such a high OH peak in the late afternoon. Suggesting a mechanism responsible for this behaviour in OH, which is not included in our model.
5.2.5 Comparison with other datasets

To get a deeper insight on the problem of the ratio of RO$_2^*$ and HO$_2$ the same simulation as described above was repeated for air masses measured over the remote Atlantic Ocean with NO$_x$ mixing ratios <20 pptv [Burkert et al., 2001b]. The simulated mixing ratios of HO$_2$ and RO$_2^*$ agree well with the measurements [Andreas Hofzumahaus et al., personal communication, 2002]. The measured H$_2$O$_2$ concentrations were also well simulated (Figure 65). The ratio between RO$_2^*$ and HO$_2$ varied around two, whereas, during the PRIME campaign the ratio reached levels up to 10. Even high amounts of NMHC (sections 5.2.3.2 - 5.2.3.7) cannot lead to such high ratios in the model.

Figure 64: Diurnal variation of measured and simulated (base case (C$_3$H$_6$ = 8500 pptv) and base case with a 10 times faster O$_3$ reaction rate) OH mixing ratios.
Figure 65: Comparison between measured and simulated H$_2$O$_2$ mixing ratios for the ALBATROSS campaign [Burkert et al., 2001b]. H$_2$O$_2$ data were measured by Weller et al. [2000].

Overview of available HO$_2$ datasets:

- **BERLIOZ**: HO$_2$ measurements with the laser induced fluorescence (LIF) technique performed by the Forschungszentrum Jülich [Hofzumahaus et al., 1998] up to 20 pptv on July 20$^{th}$ 1998 in Berlin [Platt et al., 2002]. RO$_2^+$ measurements using the PERCA technique reached levels up to 53 pptv Mihelcic et al. [2003]. The MIESR measurements of HO$_2$ and RO$_2^+$ of Mihelcic et al. [2003] are in agreement with the LIF and PERCA observations.

- **ORION99**: HO$_2$ measurements (LIF) by Kanaya et al., [2000, 2001] show mixing ratios between 10 and 25 pptv. The measurements were made at a remote island of Okinawa. Different air masses were encountered, clean marine (O$_3$ 10 ppbv, CO 90 ppbv), polluted from Japan (O$_3$ 35 ppbv, CO 100 ppbv), south-eastern
clean (O$_3$ 20 ppbv, CO 100 ppbv), polluted from China east coast (O$_3$ 30 ppbv, CO 150 ppbv), south-western (O$_3$ 20 ppbv, 110 ppbv).

- **PROPHET98**: The HO$_2$ measurements by Tan et al., [2001] used the LIF technique reached levels up to 25 pptv. The site in the northernmost part of Michigan, was located in a hardwood forest.

- **Tropospheric OH Photochemistry Experiment**: HO$_2$ mixing ratios were measured by LIF [Stevens et al., 1997, Mather, 1997, Mount et al., 1997] up to 3 pptv, the RO$_2^*$ (PERCA) measurements of Cantrell et al. [1997], which do not consider any water interference [Burkert et al., 2001b, Reichert et al., 2003], reached levels up to 40 pptv. The Idaho Hill site was located in remote mountains near Caribou, Colorado, elevation 3091 m. The measurements were taken during August and September of 1993.

- **Los Angeles free radical experiment (LAFRE)**: The experiment was situated in Claremont, California, 55 km downwind from downtown Los Angeles during September 1993 [George et al., 1999]. The HO$_2$ mixing ratios reached up to 10 pptv (FAGE).


- **ALBATROSS**: Measurements of HO$_2$ (LIF) and RO$_2^*$ (PERCA) mixing ratios reached levels up to 25 pptv and 80 pptv respectively [Andreas Hofzumahaus, personal communication, 1997, Burkert et al., 2001b]. The ALBATROSS campaign took place over the Atlantic Ocean (50°N to 40°S) in November 1996 on board the German research vessel Polarstern.
The measurements of HO$_2$ and RO$_2^*$ performed in the studies listed (Table 8) show large variabilities. Even under comparable meteorological and pollution levels the variability remains.

There are several campaigns described in the literature which also mention an overestimation of both measured RO$_2^*$ and HO$_2$ concentrations by models. These measurements of RO$_2^*$ were partly not corrected for the water interference or using an old unreliable system for the measurement of HO$_2$ with an interference of water cluster [Mount and Williams, 1997, Tanner et al., 1997, Hard et al., 1992, Stevens et al., 1994, McKeen et al., 1997, Cantrell et al., 1997].

During the PROPHET summer 1998 campaign Tan et al. [2001] observed OH, which was a factor of 2.7 underestimated by the model on average. The measured HO$_2$ concentration, however, was in good agreement with the simulations.

During the BERLIOZ campaign which took place near Berlin, Germany, in an area comparable to the region investigated during PRIME, the measured HO$_2$ mixing ratios were on average about a factor of two to four higher than the HO$_2$ mixing ratios observed during PRIME. The observed ratio between RO$_2^*$ and HO$_2$ varied between 2 and 2.5 around noon. The maximum mixing ratios of RO$_2^*$ reached up to 53 pptv at noon.

The discrepancy in the results of both campaigns is large, but to explain this by an artefact in either of the measurement techniques for HO$_2$ is inappropriate. There are still many unknowns in the composition of both encountered air masses.
5.2.6 Interpretation

The large discrepancies between the model results and the measurements of HO$_2$ and RO$_2^*$ might be explained as follows:

- There is a process which leads to a reduction of HO$_2$ and a large increase of RO$_2$. This process could be the reaction of CO with HO$_2$ in the presence of H$_2$O. The reaction rate coefficient of CO and HO$_2$ is expected to be higher in the presence of H$_2$O [Reichert et al., 2003]. The disagreement between the measured HO$_2$ and H$_2$O mixing ratios, however, can be explained if one of the pathways of this reaction leads to H$_2$O$_2$ (see reaction (151)).

\[ CO + HO_2 + H_2O \rightarrow CO_2 + OH + H_2O \rightarrow CO_2 + H + H_2O_2 \] (151)

Some studies in the past have indicated that this reaction may occur but only a very low upper limit for this reaction rate coefficient was obtained [NIST Standard Reference Database 17 and references therein, 1998]. However, an extended investigation concerning the influence of water on the reaction rate coefficient has not yet been done.

A reaction of the type just described would change the ratio between HO$_2$ and OH and would consequently lead to an enhanced oxidation of hydrocarbons due to enhanced amounts of OH, and therefore would increase the rate of production of RO$_2$.

However, the CO and H$_2$O mixing ratios measured during the BERLIOZ campaign were similar to the PRIME conditions. In addition, the fast interconversion of the RO$_2$ radicals into HO$_2$ via their reaction with NO is still dominant.

- There is another oxidising agent present like OH, for example Cl, which could lead to additional amounts of RO$_2$ and therefore to a higher ratio of RO$_2^*$ to HO$_2$. In contrast to OH, Cl does not react with CO and therefore increases the ratio between RO$_2$ and HO$_2$. The required levels of Cl to oxidise the same amounts of alkanes can be two orders of magnitude lower than OH due to the higher reactivity especially with alkanes.
It is very interesting to note that measurements of the isotopic fractionation of \(\text{CH}_4\) above the Pacific Ocean have recently provided evidence for the enrichment of the \(\text{CH}_4\) fractions, which cannot be explained by OH chemistry alone, therefore Allan et al. [2001] concluded an additional oxidant is required. The expected source could either be the ocean or halogenated organics. If the ocean is the dominant source, the differences in the measured mixing ratios of \(\text{HO}_2\) between PRIME and BERLIOZ might be explained.

As in the previous point the importance of this reaction in polluted regions should be almost negligible, unless unexpectedly high amounts of Cl are present.

- The reaction rate frequencies of \(\text{NO}\) with \(\text{RO}_2\) are substantially lower for larger \(\text{RO}_2\) than reported, i.e. the \(\text{RO}_2\) radicals produced by the oxidation of larger alkanes, alkenes, and alkynes react slower with \(\text{NO}\) than \(\text{HO}_2\) or \(\text{CH}_3\text{O}_2\). This would imply a longer lifetime of \(\text{RO}_2\). In the model used here this effect has not been taken into account due to the assumption of a propene and ethene equivalent. There has been a disagreement about the corresponding reaction rate coefficients [Eberhard and Howard, 1997, Jenkin and Hayman, 1995, Peeters et al., 1992]. However, the expected variability is too small to have an important impact on the ratio of \(\text{RO}_2^*\) to \(\text{HO}_2\).

- The FAGE system has an artefact which leads to an underestimation of the \(\text{HO}_2\) concentration by a factor of two to four. Taking this into account, the measurements of \(\text{RO}_2^*\) and \(\text{HO}_2\) are in good agreement, particularly concerning the ratio. An artefact in a measurement technique is always possible, however there is no indication for this assumption.

Overall, there is still a large disagreement between the total amounts of \(\text{RO}_2^*\) measured and simulated in the early morning hours, which cannot be solved with the current understanding of the atmospheric chemistry. The major problem is associated with the high amounts of \(\text{NO}\) present during this period of the day, together with non-negligible amounts of \(\text{RO}_2^*\) radicals. Possible explanations are:
There are high amounts of hydrocarbons present, which are produced locally and trapped in the nocturnal boundary layer. The hydrocarbons do not belong to the measured species, because the observations do not reveal any big increases in the early morning hours. These hydrocarbons have to be strongly diluted after the break up of the nocturnal boundary layer, otherwise this species would increase the RO₂* mixing ratio during the day. Such a species seems to be unlikely, but it cannot be ruled out. It has to be mentioned that enhanced amounts of 1,3 butadiene have been observed during PRIME which seems to be locally produced. However the time resolution of the hydrocarbon measurements is inappropriate to analyse the diurnal behaviour.

There is a reservoir species which builds up during the night and can easily be photolysed during the day, producing radicals. This would lead to an enhanced production of peroxy radicals in the early morning. During the day this species had no impact due to its low concentration. But during the evening the production of this species would lead to a higher loss of radicals. However, it is too speculative to name a species or describe reaction mechanisms.

In summary, there is still not a definite explanation for the observed behaviour, but the extension of the assumptions in either of the above mentioned directions is inappropriate without first having access to a more detailed set of trace gas species and some sort of characterisation of emissions from local sources.
Chapter 5: PRIME campaign

5.3 Conclusions

During the PRIME campaign an extensive set of ambient trace gas mixing ratios (RO\(_2^*\), OH, HO\(_2\), H\(_2\)O\(_2\), CH\(_3\)OOH, CO, PAN, NO, NO\(_2\)) was successfully measured. The daytime HO\(_2\) and RO\(_2^*\) measured maximum mixing ratios show levels up to 10 and 70 pptv, respectively. Maximum values were generally observed after solar noon, with HO\(_2\) and RO\(_2^*\) often persisting in significant amounts overnight.

Supporting carbonyl and hydrocarbon data are suggestive of HO\(_2\)/RO\(_2^*\) production via carbonyl photolysis and/or O\(_3\)-alkene chemistry, in addition to VOC and CO oxidation initiated by OH.

The comparison between simulations and observations showed, in particular in the early morning hours, large discrepancies in the amounts of HO\(_2\) and RO\(_2^*\). The model is not able to reproduce the peroxy radicals observed in the presence of the measured high amounts of NO\(_x\) (up to 80 ppbv) during this period of the day. Also there is no clear explanation for this phenomena, because all peroxy radicals measured by the PERCA or FAGE system are reacting with NO prior to their detection as NO\(_2\) or OH, respectively, having a lifetime of seconds.

On the other hand, if there were an additional production term not yet considered in the model, the production would have to take place exclusively in the early morning hours, otherwise the additional production term would lead to much higher peroxy radical mixing ratios later during the day. Therefore, a reservoir substance present in high amounts, is required which photolyses easily leading to additional production during the morning but then disappears later during the day. This explanation seems to be unlikely.

According to box model simulations and sensitivity studies of the radical diurnal evolution, the RO\(_2^*/\)HO\(_2\) ratios during pollution episodes vary between 1.1 and 2.3. Excluding the cases with enhanced or reduced initial NMHC concentrations of two or more orders of magnitude, the ratio varies only between 1.4 and 1.7, depending on the NMHC content of the air mass. In contrast, the measured ratios for RO\(_2^*\) and HO\(_2\), were typically in the range of 7 to 10.

The large discrepancy between measured and simulated ratios cannot be explained by the known chemistry or the presence of higher amounts of larger NMHC, according to the sensitivity study. Even 100 ppbv of a propene equivalent with a 10
times higher reaction rate with $O_3$ leads to a ratio between $RO_2^*$ and $HO_2$ of 1.5. Therefore the presence of an additional oxidising agent to the known $OH$, $O_3$, and $NO_3$ cannot be excluded.

A possible species is $Cl$ which reacts only with VOC predominantly producing $RO_2$ radicals. According to the sensitivity study even a reaction pathway which predominantly produces $RO_2$ radicals cannot result in a significant change in the ratio of $RO_2^*$ to $HO_2$, due to the presence of high amounts of NO. These high amounts of NO lead to a non linear response of the ratio of $RO_2^*$ to $HO_2$ to the ratio of VOC to CO.

Large discrepancies have also been observed between the closely linked amounts of $H_2O_2$ and $HO_2$. Assuming that $H_2O_2$ is exclusively formed by the $HO_2$ self reaction the measured $HO_2$ cannot explain the measured amounts of $H_2O_2$. Even assuming an additional production of $H_2O_2$ via the ozonolysis of VOC and the subsequent reaction of the Criegee intermediates with water vapour cannot explain this discrepancy.

A comparison of radical measurements during the BERLIOZ and PRIME campaigns shows large differences in the measured amounts of $HO_2$ in these similarly polluted regions being the $HO_2$ measured by Andreas Hofzumahaus [personal communication, 2002] a factor between 2 and 3 higher than by Dwayne Heard [personal communication, 2002].

The maximum concentrations of $RO_2^*$ in different regions and levels of pollution seem not to be strongly dependent on the origin of the air mass. However, this cannot be generalized, because observations in forested regions in Portugal showed $RO_2^*$ mixing ratios up to 260 pptv [Burkert et al., 2001a].
6 Epitome

6.1 Summary

6.1.1 Trace gas and radical behaviour [Burkert et al., 2003a]

Selected trace gas mixing ratios (i.e. peroxy radicals ($RO_2^\cdot = HO_2 + \Sigma RO_2$), non methane hydro carbons (NMHC), O$_3$, CO, HCHO, and NO) and photolysis rate coefficients of $j(NO_2)$ and $j(O(1D))$ were measured in the marine boundary layer (MBL) over the Indian Ocean. The measurements were performed during February, March, and April 1999 as a part of the Indian Ocean Experiment (INDOEX) on board the research vessel Ronald H. Brown. During the campaign air parcels having different origins and consequently variable compositions were encountered, but all air masses, including those heavily polluted with NMHC’s and aerosols, were in the regime of rapid photochemical ozone destruction. The influence of aerosols on the photolysis frequencies was investigated by comparison of measurements and results from the radiative transfer model PHOTOST; the high optical depth (up to 0.6) and low single scattering albedo of the aerosol reduces the UV flux at the surface substantially downwind of India and Arabia, causing for instance a reduction in $j(O(1D))$ by up to 40%. The diurnal behaviour of the trace gases and parameters in the MBL has been investigated by using a time dependant 0-D chemical model. Significant differences between the diurnal behaviour of $RO_2^\cdot$ derived from the model and observed in measurements were identified. The measured HCHO concentrations differed from the model results and are best explained by some missing chemistry involving low amounts of Cl. Other possible processes, describing these two effects are presented and discussed.

6.1.2 Photochemistry and radiative effects of aerosols

[Burkert et al., 2003b]

During the intensive field phase of the Indian Ocean Experiment (INDOEX) measurements of a large set of trace gases were performed on board the RV Ronald H.
Brown. The campaign took place in February-April 1999 over the Indian Ocean. Measurements of all relevant trace gases have been used within a 0-D model to simulate and analyse the observed \( \text{O}_3 \) diurnal behaviour. For most of the days, the daytime losses are very well reproduced by the model. Additionally, the possible influence of halogens on the \( \text{O}_3 \) losses is discussed.

The amount of \( \text{O}_3 \) transported to the area of observation has been analysed in more detail. Particularly, the possibility of diurnal variability in the entrainment strength of trace gases from the free troposphere into the MBL has been investigated. Also in this context, the influence of aerosols on the stability of the lower troposphere is discussed and evaluated by results from the radiative transfer model (RTM) SCIATRAN.

The results of the RTM calculations of the warming rates caused by the aerosols’ absorption of solar radiation during the INDOEX campaign showed temperature increases up to 1 K. The temperature increase particularly above the MBL stabilises the atmosphere significantly. Therefore, the presence of aerosols in the layer above the MBL leads to enhanced stability during the day and less stability during the night.

The role of macro and mesoscale processes in the photochemistry of the MBL was also investigated using \( \text{O}_3 \) soundings, tropospheric columns of \( \text{O}_3 \), \( \text{NO}_2 \), and HCHO from satellite based measurements and back trajectory analysis. During the Indian Ocean field work air masses of very different origin, and pollutant content, were encountered, for example, air masses of Southern Hemispheric pristine origin through to air masses of continental Northern Hemispheric (extra tropical) origin.

Vertical profiles of \( \text{O}_3 \) soundings show the different situations in the Northern and Southern Hemispheres. By combination of vertical profiles, satellite pictures of tropospheric columns of \( \text{O}_3 \), \( \text{NO}_2 \), HCHO, and meteorological data, it was possible to analyse the strength of strato-tropospheric exchange within the Hadley cell and the anthropogenic influences in the mid troposphere of the Northern Hemisphere (NH).

### 6.1.3 Peroxy radicals and peroxides in the urban troposphere

[Burkert et al., 2003c]

Ambient measurements of trace gases were carried out during the Peroxy Radical Initiative for Measurements in the Environment (PRIME) campaign. The data include measurements of following trace gases: hydrogen peroxy radicals (HO\(_2\)), peroxy
radicals ($\text{RO}_2^* = \text{HO}_2 + \text{RO}_2$), hydroxyl radicals (OH), hydrogen peroxide ($\text{H}_2\text{O}_2$), methyl peroxide ($\text{CH}_3\text{OOH}$), carbon monoxide (CO), peroxy acetyl nitrate (PAN), nitrogen oxide (NO), and nitrogen dioxide ($\text{NO}_2$). The measurement site was located near to London, UK, the air coming from the city centre. The campaign took place in July-August 1999.

During daylight, the maximum $\text{RO}_2^*$ mixing ratios varied between 15 and 70 pptv during “polluted episodes”. At night non negligible amounts of $\text{RO}_2^*$ were observed, varying between 5 to 20 pptv. Daytime measurements were compared with results from a box model simulation to identify differences between theory and the actual observations. Some of the model parameters were constrained to measured concentrations of trace gases to minimize the influence of transport processes.

The comparison between simulated and measured daytime trace gas concentrations showed good agreement for $\text{RO}_2^*$, $\text{H}_2\text{O}_2$, OH and large discrepancies for HO$_2$. In addition, a sensitivity analysis was run to look at variability in the amount of peroxy radicals and the influence of the ozonolysis of alkenes. The measured $\text{RO}_2^*$ to HO$_2$ ratio varied between 5 to 10, which is in total disagreement with the model results where this ratio varied between 1.1 and 2.3 even when the model was run with unrealistically high amounts of volatile organic compounds (VOC). The measured H$_2$O$_2$ mixing ratios are also in disagreement with the observed HO$_2$ amounts under the assumption that H$_2$O$_2$ is exclusively produced via the HO$_2$ self reaction.

The actual measurements of $\text{RO}_2^*$, HO$_2$, and NO taken during the early morning hours showed that these three species coexisted in high amounts. This cannot be explained by the known chemistry. A sensitivity study of the model run assuming extremely high amounts of NMHC also failed to explain this coexistence.
6.2 Conclusion

The photochemistry and the dynamics of the Earth’s atmosphere are highly complex and interlinked. Therefore it is unrealistic in this discussion to separate out either of these aspects. Even the best computers cannot solve this complex system as a whole.

The main focus of this study is to investigate processes responsible for the amounts of radicals and ozone in the atmospheric boundary layer. Analysis of short lived radicals has the advantage that dynamic processes occurring in the atmosphere have only a minor impact on their behaviour. On the other hand these short lived radicals are involved in almost all of the photochemical reaction taking place in the atmosphere. Therefore, in order to maintain the necessary photochemical complexity an essential part of this work was to develop a 0-D homogeneous gas phase chemistry model.

In addition the processes responsible for the amount of O$_3$ present in the atmosphere were analysed. O$_3$ has a moderately long lifetime and therefore neither the dynamical processes nor the photochemical processes can be neglected. To simplify the complexity of the analysis, the marine boundary layer above the Indian Ocean was selected. The study of the radical and ozone chemistry was complemented by using sonde and satellite observations to identify possible transport processes.

The present investigation is based on two field studies, one in the “clean” and the other in “polluted” atmospheres. A set of trace gases, meteorological parameters, and photolysis frequencies were successfully measured within these two types of environment.

The 0-D model developed in this study was then used to test our conventional knowledge of the atmosphere. In addition, a radiative transfer model was used and adapted to calculate the photolysis frequencies.

This study highlights several features of relevance for improving current knowledge about the Earth’s atmosphere. These are described in more detail in the following sections.
6.2.1 Evidence for Cl in the atmosphere

In recent years, some evidence for the presence of Cl in the atmosphere has been reported in the literature. Several scientists have estimated Cl concentrations in the order of $10^3$ to $10^6$ molecules cm$^{-3}$.

Within this present study, some evidence for the presence of Cl has also been found. This knowledge has been extended by combining it with further interpretation of other supporting data found in the literature. The main evidence for Cl in the atmosphere can be summarized as follows:

1. The measured diurnal behaviour of RO$_2^*$ over the Indian Ocean is observed to be significantly broader than that estimated using an OH oxidation scheme suitable for the pristine and remote MBL. This broad RO$_2^*$ or bulge shape indicates that more RO$_2^*$ is present in the early morning and late afternoon than the known OH chemistry predicts.

   The appearance of a broader RO$_2^*$ shape is not correlated with the measured amount of NMHC but can be related to the origin of the air masses. Overall this indicates the presence of missing chemistry in the model in the early morning and late afternoon. One reasonable explanation for the observed behaviour is the presence of small amounts chlorine in the MBL producing additional RO$_2^*$ by hydrocarbon oxidation (chapter 2.2.2.4). The sources of Cl are most likely to be release from sea salt aerosols and also possibly the oxidation of organic halides.

   The proposed mechanism of Cl release from aerosols have been described in detail in chapter 2.2.1.8. However, the measurements of aerosols during INDOEX indicated no correlation between the appearance of the bulge in the RO$_2^*$ behaviour with the appearance of maxima in either the total number of aerosols or levels of acidity [Ball et al., 2003]. The Cl release of aerosols is predicted to be catalysed by higher levels of acidity.

2. The high HCHO mixing ratios measured by Wagner et al., [2001] during the INDOEX campaign suggested the presence of another oxidising agent like OH. If present, Cl would lead to additional amounts of RO$_2^*$ and therefore to higher
concentrations of HCHO. The required level of Cl was estimated in this work to be in the order of $1 \times 10^4$ to $1 \times 10^5$ molec cm$^{-3}$ (section 4.2.3.2).

3. The observed relationship between the daily measured maximum mixing ratios of CO, HCHO, and RO$_2^*$ during INDOEX indicates a close chemical link between these species. This link cannot be well explained by the known OH oxidation chemistry used in the 0-D model. The most likely explanation of this behaviour is the presence of Cl in the MBL (section 4.2.3.2.2).

4. Recent measurements of the isotopic fractionation of CH$_4$ above the Pacific Ocean by Allan et al. [2001] have provided evidence for the enrichment of CH$_4$ fractions, which cannot be explained by OH chemistry alone. An additional oxidant such as Cl is required.

5. The measurements of Cl$_2$ [Spicer et al., 1998] in a coastal region of the eastern USA showed high amounts of Cl$_2$ during the night (up to 150 pptv). Photolysis in the early morning therefore has to produce Cl concentrations of up to $1.3 \times 10^5$ atoms cm$^{-3}$. The source of the inorganic Cl$_2$ is presumably multi-phase reactions involving aerosols.

6. Lagrangian experiments (i.e. measurement at two sides upwind and downwind, or in a plume with aircrafts and mobile laboratories) including measurements of hydrocarbons have been used to estimate the concentrations of OH. These estimated OH amounts differ depending on the hydrocarbon group used for the calculation (i.e. alkanes, alkenes, or aromates).

Using Lagrangian experiments, Kramp et al., [1994] calculated OH concentrations between $5.5$ and $8.5 \times 10^6$ molecules cm$^{-3}$. Their study investigated the transport processes between Kappel (upwind) and Schauinsland (TOR-station, downwind). For the OH calculations some alkenes (isoprene and 1-hexene) were excluded, because the corresponding calculated OH was much lower than the average obtained from the other hydrocarbon measurements.
The same behaviour was observed by Klemp et al., [1993] calculating OH concentration of \(2 \times 10^6\) molecules cm\(^{-3}\) from long-term measurements of C3-C5 alkanes. The measurement stations were at Lyon and Schauinsland with an average transport time of about 28 hrs. As a consequence, the estimated OH concentrations have a much higher uncertainty than the values by Kramp et al., [1994] (transport time \(\sim 3\) hrs). However, the calculations considering the measured alkene concentrations (ethane, propene, 1-butene) lead likewise to much lower OH concentrations.

Blake et al. [1993] estimated OH concentrations from airborne VOC measurements in the London plume (London Photochemical Plume Experiment). They estimated twice the concentration of OH from their [aromate]/[acetylene] measurements (day 1 OH = \((3.0 \pm 0.3) \times 10^6\) molec cm\(^{-3}\) and day 2 \((9.4 \pm 1.4) \times 10^6\) molec cm\(^{-3}\)) as they did from their [alkene]/[acetylene] measurements (day 1 \((1.7 \pm 0.4) \times 10^6\) molec cm\(^{-3}\) and day 2 \((4.1 \pm 1.0) \times 10^6\) molecules cm\(^{-3}\)). They proposed an additional loss process for the aromates, not involving OH in the destruction cycle. In addition, they found that their measured alkanes showed the same behaviour as the aromates.

In the studies presented so far, the ozonolisis of alkenes has been neglected in the calculations of OH because it accounts only for approximately 5% of the total destruction of alkenes and therefore would lead to an overestimation of the OH concentration.

None of the above mentioned authors reported any obvious explanation for these discrepancies in the calculated amount of OH.

However, taking into account the knowledge recently gained and reported on this thesis, discrepancies in the calculated amount of OH can be explained, if Cl is present in sufficient amounts. In general, \(k_{Cl}/k_{OH}\) ratio vary between 60 and 230 for the alkanes and between 4 and 14 for the alkenes (Table 9). Thus being predicated on the assumption that approximately 50% of the alkanes are oxidised by Cl and that \(k_{Cl} \sim 10^2 \times k_{OH}\), (i.e. \([OH] = 2 \times 10^6\) molecules cm\(^{-3}\) (50%) and \([Cl] \sim 1 \times 2 \times 10^4\) molecules cm\(^{-3}\) (50%)) the total losses of the alkanes would be the same as calculated with the double amount of OH, and in agreement with the observations given by Kramp et al. [1994].
Additionaly the corresponding theoretical total losses of the alkenes would be approximately 40% lower, i.e. the total calculated loss of alkenes consists of 50% by OH and 10% by Cl (as the reaction of Cl with alkenes proceeds more slowly).

In this manner, i.e. assuming that the Cl concentration is two orders of magnitude lower than OH, and taking into account the different reactivity of alkanes and alkenes with Cl, both alkane and alkene measurements would lead to the same estimated concentration of OH.

<table>
<thead>
<tr>
<th></th>
<th>Cl $k_{298K}$ ($10^{11}$ cm$^3$ molec$^{-1}$ s$^{-1}$)</th>
<th>OH $k_{298K}$ ($10^{11}$ cm$^3$ molec$^{-1}$ s$^{-1}$)</th>
<th>NO$<em>3$ $k</em>{298K}$ ($10^{17}$ cm$^3$ molec$^{-1}$ s$^{-1}$)</th>
<th>O$<em>3$ $k</em>{298K}$ ($10^{13}$ cm$^3$ molec$^{-1}$ s$^{-1}$)</th>
<th>$k_{Cl}/k_{OH}$</th>
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Table 9: Reaction rate coefficients for Cl, OH, NO$_3$, and O$_3$ with VOC [Finnlayson-Pitts and Pitts, 2000].
7. The analysis of long term measurements at the Schauinsland site in Germany, showed higher alkene/i-butane ratios during summer than in winter. Due to the more intense photochemistry during summer the opposite effect would be expected. Klemp et al., [1993] proposed additional biogenic sources for smaller alkenes (C2-C4) which they assumed overcompensates for the higher losses during summer relative to the alkanes. Isidorov et al. [1985] and Sawada and Totsuka [1986] reported biogenic emissions of smaller olefins.

As already stated, Cl is more reactive with alkanes than with alkenes relative to their reaction with OH, therefore this different alkene/i-butane ratios can also be explained by the presence of Cl in the following way. Provided that Cl is produced by the photodissociation of a reservoir substance XCl (e.g. CHOCl) and the photodissociation energy is higher than for O$_3$, HONO, and HCHO, then the ratio (Cl production / OH production) would be higher in summer than in winter. As a consequence the ratio Cl/OH is higher in summer and the alkanes are removed more efficiently than the alkenes in the summer scenario i.e., more i-butane is removed relative to the alkenes in the summer than in the winter scenario.
8. There is ongoing discussion about “missing HOx” in the free troposphere (i.e. measured HOx 2-4 times larger than predicted from primary OH production).

Figure 66: Relative fluxes in the free troposphere calculated by Nic Carslaw – U. York., UK using the Master Chemical Mechanism (MCM, Uni-Leeds)

One possible role for Cl has however not yet been considered in the analysis. Provided that 60% of HO2 in the free troposphere is produced via RO as illustrated by Figure 66, then Cl might explain the difference of simulated and measured HOx mixing ratios. Assuming the long-lived alkanes are homogenously vertically distributed throughout the middle and lower troposphere, in contrast to the shorter lived alkenes. Then the presence of sufficient levels of Cl could lead to an additional production of RO by oxidation of hydrocarbons and subsequently to HO2.

The above mentioned arguments support the presence of Cl, however the possible origins still remain as an open question. As described below, there are several sources of Cl already mentioned or excluded in the literature. In addition, the mentioned evidences for the presence of Cl characterise the possible sources of Cl.
Several studies [Khalil and Rasmussen, 1999, Moore et al., 1996] have shown that the ocean is not a significant source of CH$_3$Cl. Yokouchi et al. [2000] observed up to 2100 pptv of CH$_3$Cl on islands in the tropics, but these high mixing ratios might be related to emissions from forested land.

Spicer et al. [1998] suggested multi-phase reactions involving aerosols as a possible source of Cl$_2$, which is easily photodissociated producing Cl.

Calculating the production of Cl via the oxidation of halogenated hydrocarbons (see section 2.2.2.4.3) yield to an upper limit of [Cl] = 5.9x10$^3$ [atoms cm$^{-3}$], for an [OH] = 1x10$^7$ [molecule cm$^{-3}$] and mixing ratio of CH$_4$ = 1.8 ppmv, i.e. apparently too small to produce significant amounts of Cl. However, the total oxidation of all present halogenated hydrocarbons might increase the calculated upper limit.

In conclusion, the possible source(s) of Cl remain unclear, but the variety of regions, where indications for the presence of Cl was found gives evidence for the ubiquity of Cl. Heterogeneous production mechanisms seem therefore to be unlikely. Taking into account their long lifetime and homogeneous distribution throughout the atmosphere, halogenated hydrocarbons might be the most likely source of Cl.

To summarise this discussion I conclude, perhaps provocatively given the potential consequence of this finding on the chemistry of the Earth’s atmosphere, that:

“Cl is present in the whole atmosphere in levels between 1x10$^4$ and 1x10$^5$ molecule cm$^{-3}$. The sources of Cl are ubiquitous and most likely halogenated hydrocarbons. This results in a oxidising capacity of Cl comparable to that of OH in particular in reactions with the alkanes. This would imply that the “cleansing efficiency of the atmosphere” is significantly higher than expected from conventional models. The OH radical would no longer be the “detergent” of the atmosphere. Lifetimes of hydrocarbons would be significantly reduced and strategies to increase air quality would have to be rethought.”
6.2.2 Influence of aerosol absorption in the dynamics of the atmosphere

In the present study the results of the RTM calculation of warming rates (i.e. caused by the aerosols' absorption of solar radiation during the INDOEX campaign) showed temperature increases up to 1 K within the aerosol layer (1-3km). This has a significant effect in the stability of the atmosphere. The presence of aerosols in the layer above the MBL leads to enhanced stability during the day and less stability during the night and therefore to a diurnal variation in the entrainment strength.

This work has shown the necessity reconsidering the parameterisation of convective processes in all models to account for the impact of aerosols in atmospheric dynamics.

6.2.3 Importance of the STE as a source of O₃ over the Indian Ocean

The interpretation of vertical O₃ profiles in the SH and satellite data of a variety of trace gases above the Indian Ocean has shown that stratospheric O₃ can be the major source of tropospheric O₃. Satellite data indicated no influence of biomass burning or lightning produced NOₓ in the area of observation. In spite of the distant location of other possible sources (due to the long lifetime of O₃ in the middle and upper troposphere) their influence cannot completely ruled out. However, back trajectory analysis showed that transport processes from polluted regions was unlikely.

Taking all the data into account it appears that the amount O₃ resulting from the STE is the major source for tropospheric O₃ in the SH Indian Ocean during February and March. Therefore these data provide adequate information for the quantification of the stratospheric contribution.

Additionally this dataset also gives an excellent opportunity to analyse the reliability of global models in the SH Indian Ocean region. Further comparisons of the data collected with model results are recommended.
6.2.4 Open questions in the radical chemistry of the "polluted" atmosphere

Coexistence of NO\textsubscript{x} and RO\textsubscript{2}\textsuperscript{*}

In this study comparison between the results of model simulations and actual observations showed, especially in the early morning hours, large discrepancies in the amounts of HO\textsubscript{2} and RO\textsubscript{2}\textsuperscript{*}. The model is not able to reproduce the peroxy radicals observed in the presence of the measured high amounts of NO\textsubscript{x} (up to 80 ppbv) during this period of the day.

There is no easy explanation for this phenomena, due to the short lifetime of the peroxy radicals (~seconds). On the other hand, if there were an additional production term not yet considered in the model, this should be activated only in the early morning hours, in order to prevent the additional production of peroxy radicals later during the day. Therefore, high amounts of a reservoir substance which photolyses easily, and which leads to additional radical production during the morning but disappears later during the day is required. The existence of such a substance seems to be unlikely.

Unexplainable RO\textsubscript{2}\textsuperscript{*}/HO\textsubscript{2} ratios

According to box model simulations and sensitivity studies of the radical diurnal evolution, RO\textsubscript{2}\textsuperscript{*}/HO\textsubscript{2} ratios during pollution episodes are expected to vary between 1.1 and 2.3. Excluding cases with enhanced or reduced initial NMHC concentrations of two or more orders of magnitude, the ratio varies only between 1.4 and 1.7, depending on the NMHC content of the air mass. By contrast, the actual RO\textsubscript{2}\textsuperscript{*}/HO\textsubscript{2} ratios measured in this study were typically in the range of 7 to 10.

This large discrepancy between measured and simulated ratios cannot be explained by any known chemistry.

Sensitivity studies have shown that the maximum RO\textsubscript{2}\textsuperscript{*} and HO\textsubscript{2} mixing ratios vary only slightly. Therefore, the ratio between max RO\textsubscript{2}\textsuperscript{*} and max HO\textsubscript{2} under heavily polluted conditions is expected to be constant. This steady ratio seems to be caused by fast reactions with NO which dominate the loss and/or interconversion of peroxy radicals, which leads to peroxy radical lifetimes of a few seconds. The presence of an additional oxidising agent to the known OH, O\textsubscript{3}, and NO\textsubscript{3} cannot be excluded, but seems unlikely.

Inconsistency between HO\textsubscript{2} and H\textsubscript{2}O\textsubscript{2} measurements
Large discrepancies have been observed in this study between the closely linked amounts of H$_2$O$_2$ and HO$_2$. Assuming that H$_2$O$_2$ is formed exclusively by the HO$_2$ self reaction, then the actual levels of HO$_2$ measured cannot explain the measured amounts of H$_2$O$_2$. Even some additional production of HO$_2$ via the ozonolysis of VOC and the subsequent reaction of the Criegee intermediates with water vapour cannot explain this discrepancy.
6.3 Outlook

The results of this study have shown some deficits in the current physicochemical description of the processes occurring in the Earth’s atmosphere.

The results obtained with the developed 0-D model for the “clean” and “polluted” atmospheric boundary layer have indicated that the radical and O\textsubscript{3} chemistry is insufficiently understood. Limitations of available computing time require simplifications which are inadequate to identify new processes with a high accuracy. In addition, measurement techniques need to be improved to get both a higher confidence and a more detailed dataset.

Direct detection of Cl is desirable to quantify to what extent Cl oxidises hydrogen-containing gases, however the requirements to improve the current measurement techniques to detect Cl with sufficient accuracy seem to present insurmountable difficulties, at least with current technologies. A possible alternative would be to measure a directly linked species like ClO or Cl\textsubscript{2} to achieve on short term scale the required information.

The absorption of solar radiation by aerosols and the possible large impacts on the local dynamics is poorly understood. Further research is required for a better physical description of the optical behaviour of the aerosols.

The results of the investigation of a polluted part of the Earth’s atmosphere poses the question of how reliable are predictions from existing large scale models, when the chemical processes are relatively poorly understood. In particular the lack of clear understanding of “fast photochemistry”, (i.e. photochemical reactionswhere it is appropriate to neglect transport processes), where I have found dramatic discrepancies between my simulations and actual measurements.
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Acknowledgements

Foremost, I would like to thank my two advisors Prof. Dr. John Phillip Burrows and Prof. Dr. Russell R. Dickerson for their interest, support, and encouragement. Although, we rarely had the same opinion, but the numerous discussions with both John and Russ were of great benefit, hopefully not only for myself. The best thing I got to know was the fact that they always treated me with respect and never patronizing me. I am deeply indebted to Prof. John Phillip Burrows for giving me the opportunity from the beginning of my scientific career till now to be involved in so many national and international campaigns and to visit so many interesting international conferences. Many thanks to Prof. Dr. Russel R. Dickerson for inviting me to Maryland to discuss several issues and to get to know all the staff.

I also would like to thank Dr. Maria Dolores Andrés Hernández for many many fruitful discussions and for her encouragement. The most important thing I learned from her was bringing things to the end and being more disciplined.

I wish to thank Lars Reichert for helpful discussions and many experience which we made together during several campaigns.

I would like to thank my lovely girlfriend Birgit Behnke for her patience and her believing in me, giving me a big support.

Finally, I would like to thank my parents, Karla and Eckhard, and my grandparents Liselotte und Richard for their inexpressible love and support throughout my whole life. Everyone should have such a wonderful family, all my gratitude to you.

Ich liebe Euch.
Appendix 1

Derivation of $\frac{d[O_3]}{dt} = k_{NO+HO_2}[NO][HO_2] + k_{NO+RO_2}[NO][RO_2]$

In the lower troposphere the chemical reactions, which determine the amount of ozone are currently understood to be

\begin{align*}
NO + O_3 & \rightarrow NO_2 + O_2, \ k_1 \\
NO_2 + hv \ (\lambda < 420 \ nm) & \rightarrow NO + O(3P), \ j_2 \\
O(3P) + O + M & \rightarrow O_3 + M, \ k_3 \\
NO + HO_2 & \rightarrow NO_2 + OH, \ k_4 \\
NO + RO_2 & \rightarrow NO_2 + RO, \ k_5 \\
OH + O_3 & \rightarrow HO_2 + O_2, \ k_6 \\
HO_2 + O_3 & \rightarrow OH + 2 \cdot O_2, \ k_7 \\
O_3 + hv \ (\lambda < 320 \ nm) & \rightarrow O(1D) + O_2, \ j_8 \\
O(1D) + H_2O & \rightarrow OH + OH, \ k_9 \\
O(1D) + N_2 & \rightarrow O(3P) + N_2, \ k_{10} \\
O(1D) + O_2 & \rightarrow O(3P) + O_2, \ k_{11} \\
OH + NO_2 + M & \rightarrow HNO_3 + M, \ k_{12} \\
OH + CO & \rightarrow COOH, \ k_{13} \\
COOH + O_2 & \rightarrow HO_2 + CO_2, \ k_{14} \\
OH + RH & \rightarrow R + H_2O, \ k_{15} \\
R + O_2 + M & \rightarrow RO_2 + M, \ k_{16} \\
RO + O_2 & \rightarrow R + O + HO_2, \ k_{17} \\
O(3P) + NO_2 & \rightarrow NO + O_2, \ k_{18}
\end{align*}
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For simplicity reasons the reactions of O\(_3\) with alkenes and other likely important reactions of VOC are negelcted.

Unlike in the troposphere the concentration of O atoms is sufficiently small that reaction 18 is of negligible importance in the troposphere. The time dependent variation of O\(_3\), O\(^{(3)P}\), and O\(^{(1)D}\) is therefore given by

\[
\frac{d[O_3]}{dt} = k_3 \left[ O^{(3)P} \right] [O_2] [M] - k_{11} [NO][O_3] - k_6 [OH][O_3] - k_7 [HO_2][O_3] - j_8 [O_3], \text{ eq. 1}
\]

\[
\frac{d[O^{(3)P}]}{dt} = j_2 [NO_2] + k_{10} \left[ O^{(1)D} \right] [N_2] + k_{11} \left[ O^{(1)D} \right] [O_2] - k_3 \left[ O^{(3)P} \right] [O_2] [M], \text{ eq. 2}
\]

\[
\frac{d[O^{(1)D}]}{dt} = j_8 [O_3] - k_{10} \left[ O^{(1)D} \right] [N_2] - k_{11} \left[ O^{(1)D} \right] [O_2] - k_9 \left[ O^{(1)D} \right] [H_2O], \text{ eq. 3.}
\]

Assuming that the reactive oxygen atoms achieve a stationary state i.e. \(\frac{d[O^{(1)D}]}{dt} = 0\), and \(\frac{d[O^{(1)D}]}{dt} = 0\) yields,

\[
k_3 \left[ O^{(3)P} \right] [O_2] [M] = j_2 [NO_2] + k_{10} \left[ O^{(1)D} \right] [N_2] + k_{11} \left[ O^{(1)D} \right] [O_2], \text{ eq. 5}
\]

\[
k_{10} \left[ O^{(1)D} \right] [N_2] + k_{11} \left[ O^{(1)D} \right] [O_2] = j_8 [O_3] - k_9 \left[ O^{(1)D} \right] [H_2O], \text{ eq. 6}
\]

Substituting eq 5 and 6 into the rate of formation of O\(_3\) yields the following:

\[
\frac{d[O_3]}{dt} = j_2 [NO_2] + k_{10} \left[ O^{(1)D} \right] [N_2] + k_{11} \left[ O^{(1)D} \right] [O_2] - k_1 [NO][O_3] - k_6 [OH][O_3] - k_7 [HO_2][O_3] - j_8 [O_3] \text{, eq. 7}
\]

\[
\frac{d[O_3]}{dt} = j_2 [NO_2] + j_8 [O_3] - k_9 \left[ O^{(1)D} \right] [H_2O] - k_1 [NO][O_3] - k_6 [OH][O_3] - k_7 [HO_2][O_3] - j_8 [O_3] \text{, eq. 8}
\]

\[
\frac{d[O_3]}{dt} = j_2 [NO_2] - k_9 \left[ O^{(1)D} \right] [H_2O] - k_1 [NO][O_3] - k_6 [OH][O_3] - k_7 [HO_2][O_3], \text{ eq. 9}
\]
where \( k_9 [O('D)][H_2O] \) is the amount of \( O('D) \) which produces OH radicals.

Assuming further, that NO\(_2\) achieves a stationary state i.e. \( \frac{d[NO_2]}{dt} = 0 \),

\[
\frac{d[NO_2]}{dt} = k_1 [NO][O_3] + k_4 [NO][HO_2] + k_5 [NO][RO_2] - j_2 [NO_2] - k_{12}[OH][NO_2][M], \text{ eq. 10}
\]

then

\[
j_2 [NO_2] = k_1 [NO][O_3] + k_4 [NO][HO_2] + k_5 [NO][RO_2] - k_{12}[OH][NO_2][M], \text{ eq. 11.}
\]

Including equation eq. 11 into equation eq. 9 results in:

\[
\frac{d[O_3]}{dt} = k_1 [NO][O_3] + k_4 [NO][HO_2] + k_5 [NO][RO_2] - k_{12}[OH][NO_2][M] - k_9 [O('D)][H_2O] - k_1 [NO][O_3] - k_6 [OH][O_3] - k_7 [HO_2][O_3], \text{ eq. 12}
\]

\[
\frac{d[O_3]}{dt} = k_4 [NO][HO_2] + k_5 [NO][RO_2] - k_{12}[OH][NO_2][M] - k_9 [O('D)][H_2O] - k_6 [OH][O_3] - k_7 [HO_2][O_3], \text{ eq. 13}
\]

but

\[
\left[ O('D) \right] = \frac{j_8 [O_3]}{k_{10}[N_2] + k_{11}[O_2] + k_9[H_2O]}
\]

thus

\[
\frac{d[O_3]}{dt} = k_4 [NO][HO_2] + k_5 [NO][RO_2] - k_{12}[OH][NO_2][M] - \frac{j_8 [O_3]k_9[H_2O]}{k_{10}[N_2] + k_{11}[O_2] + k_9[H_2O]} - k_6 [OH][O_3] - k_7 [HO_2][O_3]
\]

Finally, shows that the production \( O_3 \) is given by
In the above analysis, the following processes have not been taken into consideration

a) additional chemical loss e.g. the potential reaction of halogen atoms with O$_3$

b) the physical processes such as, the deposition of O$_3$, advection in and out of the region and entrainment from above.
Appendix 2

The following figures show the hierarchic structure of the BRAPHO and PHOTOST model. In addition the available reactions are shown which are separated into bimolecular, termolecular, and photolysis reactions.

Appendix figure 1: Overview of the BRAPHO model concept.
Appendix figure 2: Overview of the PHOTOST model concept.
<table>
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<tr>
<th>Reaction</th>
<th>Premix</th>
<th>Products</th>
<th>Rate Constant</th>
<th>Activation Energy</th>
<th>Notes</th>
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<td>( \text{OH} + \text{H}_2 \text{O} \rightarrow \text{O}_2 + \text{H}_2 \text{O} )</td>
<td>8.00E-12</td>
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<td>( \text{OH} + \text{OH} \rightarrow \text{H}_2 \text{O} + \text{O} )</td>
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<td>( \text{NH}_3 + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2 )</td>
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<td>( \text{CO}_2 + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2 )</td>
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<td>( \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2 \text{O} )</td>
<td>1.35E-10</td>
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<td>Joern(HITR, methanep Fad)</td>
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<tr>
<td>( \text{CH}_4 + \text{CH}_2 \text{O} \rightarrow \text{N}_2 + \text{O}_2 )</td>
<td>1.50E-11</td>
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# Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling

IUPAC (ASAD). L+reaction is used to get a feeling for the importance of this Master Rate File: Joern Burkert 04.07.00. All reactions are from both jpl97 JPL 1997 BIMOLECULAR REACTIONS - MASTER RATEFILE

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### General comments

- **C**: temperature dependent branching ratio based on ratio at 298 K.
- **B**: branching ratio assumed equal for all channels.

### NOTES:

- **U**: user strongly advised to consult source material.
- **U?**: branching ratio assumed equal for all channels in the absence of more information.
- **U**: branching ratio assumed equal for all channels in the absence of more information.
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Appendix

U - upper limit for rate coefficient
LT- lower limit for temperature
tn - normal form assumed (rather than iso-)
in the absence of more information
*** - products of the reactions are given by Joern Burkert 04.07.00.

Specific comments
b1 - branching ratio for ClO+HDO->HDO+O2/ClO+H2O - second branch has an upper limit of between 0.3-1.5 %. Set to zero here but retained in ratefile in case a non-zero value is determined later.
b2 - branching ratio for ClO+HDO->HDO+O2/ClO+H2O - IUPACIV states that the first branch will dominate at temperatures less than 300 K second branch is not in ratefile but should be implemented in case a non-zero value is determined later.
b3 - branching ratio for MeOOH+MeOO+ MeOH+HCHO+O2/Me+MeOH+O2/MeOOMe+O2/MeOOH+Cl2O2 in 0.61:0.31:0.1:0.0 at 298 K according to JPL94.
b4 - branching ratio for OH+ClO->HCl+O2/ClO+O2. DB + ClO. The recommended value is based on a fit to the 219-373 K data of Hilla and Howard [871], the 243-298 K data of Burrows et al. [231], and the 298 K data of Poulet et al. [1273]. Data reported in the studies of Ravishankara et al. [1300], and Leu and Lin [949] were not used in deriving the recommended value because in these studies the concentration of ClO was not determined directly. The results of Burrows et al. are temperature-independent while those of Hilla and Howard show a slight negative temperature dependence. The fraction of total reaction yielding HO2 + Cl as products has been determined by Leu and Lin (0.65); Burrows et al. (0.85±0.2); Hills and Howard (0.86±0.14); and Poulet et al. (0.98±0.12). The latest study gives an upper limit of 0.14 for the branching ratio to give HOCl + O2 as products. Even though uncertainties in all studies allow for the HOCl yield to be zero, none of the current measurements can exclude a small, but atmospherically significant, yield of HOCl. Quantification of the HOCl yield, especially at temperatures close to 200 K, is needed and set to zero here but retained in ratefile in case a non-zero value is determined later.
b5 - NO2 + N2. The existence of the reaction channel forming NO + NO2 + O2 has not been firmly established. However, studies of N2O5 thermal decomposition that monitor NO2 (Daniels and Johnston; Johnston and Tad; Cantrell et al.) and N2 (R)north et al., and Cantrell et al. require reaction(s) that decompose N3O into NO + O2. The rate constant from the first three studies is obtained from the product Keq where Keq is the equilibrium constant for NO2 + N2 = N2O5 while for the latest two studies the rate constant is obtained from the ratio k(k(ND2 + N2)) where k(ND2 + N2) is the rate constant for the reaction NO + N2 + O2 /N2O. Using Keq and k(NO + N2) from this evaluation, the rate expression that best fits the data from all five studies is 4.5 x 10-16 exp(-1260/T) cm molecule-1 s-1 with an overall uncertainty factor of 2.
b6 - Cl + CH3Cl. New Entry. Stickel et al. have used laser photolysis resonance fluorescence to measure the rate constant between 240-421 K over the pressure range of 3-700 Torr. The rate constant is near collisional but increases with increasing pressure from a low pressure limit of 1.8x10-10 to a value of 3.3x10-10 at 700 Torr. The yield of ClI at 297 K was measured using diode laser spectroscopy to drop from near unity at low pressure to a value of approximately 0.5 at 203 Torr, indicating that stabilization of a (CH3)2SCl adduct becomes competitive with hydrogen atom abstraction with increasing pressure. These investigators also observe a negative temperature dependence for the reaction. A room temperature measurement at 740 Torr by Nielsen et al. agrees with the results of Stickel et al. Set to zero here.

Pressure dependent reactions - require extra code in model to calculate rate coefficients - see source material
P1 - OH + CO -> H + CO2 k=x(10.467*Kbar)
P2 - HO + HONO2 -> H2O + NO3 (1.500E-13 = rate at 1 bar & 298 K) Generally, k(x(T))=k(298/T) where k(298/K) is the rate constant at 298 K and k(T) is the rate constant at temperature T. The rate expression is k=4.1e-16 exp(1440/T) cm3s-1 where [M] is the concentration of H2O. See JPL 1994 and the paper it references: R.R.Lii et al, J.Phys.Chem 85, 1981, p2833. This reaction (and the trimolecular branch) need to be multiplied by the following factor:
(1 + 1.40E-21[H2O]exp(1755/T)/)

Other dependencies:
D1 - Depends on the concentration of H2O. See JPL 1994 and the paper it references: R.R.Lii et al, J.Phys.Chem 85, 1981, p2833. This reaction (and the trimolecular branch) need to be multiplied by the following factor:
(1 + 1.40E-21[H2O]exp(1755/T)/)

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**Appendix**
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Notes:

Not all JPL 97 reactions are listed. Only the important ones! The thermal decay reaction has to follow the trimolecular reaction in order to be sure that the rate coefficient is calculated correctly!!

The NO2 NO2 reaction was removed, due to the implementation in the main program.
# PROTONYLYSIS REACTIONS - MASTER RATEFILE
# JPL 1994
# Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling
# and some additional reactions

# All Cross-Sections and quantum yields taken from JPL 97 unless noted
# # Cross-Sections and quantum yields taken from JPL 97

91 O2  PHOTON  O2  EJPL  MCM51
90 O2  PHOTON  O2  EJPL  MCM51
89 O2  PHOTON  O2  EJPL  MCM51
88 O2  PHOTON  O2  EJPL  MCM51
87 O2  PHOTON  O2  EJPL  MCM51
86 O2  PHOTON  O2  EJPL  MCM51
85 O2  PHOTON  O2  EJPL  MCM51
84 O2  PHOTON  O2  EJPL  MCM51
83 O2  PHOTON  O2  EJPL  MCM51
82 O2  PHOTON  O2  EJPL  MCM51
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4 O2  PHOTON  O2  EJPL  MCM51
3 O2  PHOTON  O2  EJPL  MCM51
2 O2  PHOTON  O2  EJPL  MCM51
1 O2  PHOTON  O2  EJPL  MCM51

Specific comments
b0 - Parameterisation for the Br-Bands taken from Minschwaner, JGR (1992), 97, p. 10103 - 10108, Herzberg continuum values taken from Yoshino et al.
b1 - Cross Sections taken from the MPI compilation, measured by Bass, Johnston, WMO 1975 ??
Mathematical expression for the Quantum Yields taken from JPL 97-4, P.152
b2 - Cross Sections taken from the MPI compilation, measured by Bass, Johnston, WMO 1975 ??
For the quantity yield 5 choices can be made in Phototcs (\texttt{\textbackslash{photoreacts.par}}):
1) JPL 94
2) From preprint of G. Hancock, 1994, GRL, 22, 1995, 1213-1216
3) Mihelsen et al., GRL, 21, 1994, 2227-2230
4) JPL 97
5) Talukder et al., Preprint
b3 - Cross Sections taken from Minschwaner, JGR, 1993, 98, 20401-20412
b4 - Cross Sections from Schneider et al. (MPI), temperature dependency from JPL 97, quantum yield from JPL 97
b5 - Different choices are possible in \texttt{\textbackslash{photoreacts.par}}:
- Quantum yields from Johnston, R.S. et al., J Phys. Chem., 100, 4713, JPL 97 recommendation
b6 - Quantum yield for NO3 is unity, but the other products can have different quantum yield (JPL)
b7 - 2 Choices can be made (\texttt{\textbackslash{photoreacts.par}}):
- Cross Sections taken from the Gemetran Database,
measured by R. Meller, MPI Mainz, no T dependence
- JPL 97 including T dependence

b8 - Mainz Chemie-Modell benutzt CH3OOH -> HCHO + OH + H

b9 - Cross Sections taken from Gometra Database, measured by Simon et al.

b10 - Cross Sections from Simon PhD-Thesis 1989 (236.8 - 319.0 nm)
and JPL 92-20, p. 127 (319 - 500 nm)

b11 - Cross Section taken from A. Wahner

b12 - 3 choices can be made for the Cross Sections in PhotoGT ('photoreacts.par'):
1) JPL 94
3) Deters, 1997, unpublished

recommended by JPL 97


b15 - 2 choices can be made for the Cross Sections in PhotoGT ('photoreacts.par'):
2) Deters et al., 1996, Ann Geophysicae, 468-475

b16 - 3 choices can be made for the Cross Sections in PhotoGT ('photoreacts.par'):
2) Deters et al., 1996, Ann Geophysicae, 468-475
3) JPL 97

b17 - 2 choices can be made for the Cross Sections in PhotoGT ('photoreacts.par'):
1) Ravishankara, 1996
2) Himmelmann et al., 1997

b18 - Cross Sections taken from Atkinson et al.,
Products taken from Jens-Uwe Gross, Dissertation

b19 - Cross Sections and quantum yields from Atkinson et al.,
This reaction is only in the troposphere relevant!

NICHT IMPLEMENTIERTE REKTIONEN aus JPL !!!!

- HO2 + hn . products
- NB3 + hn . N2 + H(1)
- CO + hn . C + O (1)
- CO2 + hn . CO + O (1)
- CH4 + hn . products (2)
- CH3O2 + hn . products
- CH2SO2 + hn . products
- CH3CN + hn . products
- CH3CN + hn . products
- ClO3 + hn . products
- Cl2O3 + hn . products
- Cl2O4 + hn . products
- Cl2O6 + hn . products
- HF + hn . H + F
- CINO + hn . Cl + NO
- CCIF2 + hn . products
- CF2ClCF12 + hn . products
- CF21ClCF21 + hn . products
- CF2ClCl12 + hn . products
- CF4 + hn . products
- CF6 + hn . products
- CI2 + hn . products
- CCIF4 + hn . products
- C2FO + hn . products
- CF2O + hn . products
- CH3Cl + hn . products
- CH3CCl3 + hn . products
- CH3CF2Cl + hn . products
- CH3CFCl2 + hn . products
- CF3CFCl1 + hn . products
- CF3CF2Cl1 + hn . products
- CF3CF2Cl2 + hn . products
- CF3Cl1 + hn . products
- CF3Br1 + hn . products
- CF3I1 + hn . products
- SO2 + hn . SO + O
- R2S + hn . RS + H (1)
- CS2 + hn . CS + S
- DOS + hn . CO + S
- SF6 + hn . products
- NaOH + hn . Na + OH
- NaCl + hn . Na + Cl

NICHT IMPLEMENTIERTE REKTIONEN aus JPL !!!!

- HO2 + hn . products
- NB3 + hn . N2 + H(1)
- CO + hn . C + O (1)
- CO2 + hn . CO + O (1)
- CH4 + hn . products (2)
- CH3O2 + hn . products
- CH2SO2 + hn . products
- CH3CN + hn . products
- CH3CN + hn . products
- ClO3 + hn . products
- Cl2O3 + hn . products
- Cl2O4 + hn . products
- Cl2O6 + hn . products
- HF + hn . H + F
- CINO + hn . Cl + NO
- CCIF2 + hn . products
- CF2ClCF12 + hn . products
- CF21ClCF21 + hn . products
- CF2ClCl12 + hn . products
- CF4 + hn . products
- CF6 + hn . products
- CI2 + hn . products
- CCIF4 + hn . products
- C2FO + hn . products
- CF2O + hn . products
- CH3Cl + hn . products
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- CH3CF2Cl + hn . products
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- CF3CF2Cl1 + hn . products
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- CF3Cl1 + hn . products
- CF3Br1 + hn . products
- CF3I1 + hn . products
- SO2 + hn . SO + O
- R2S + hn . RS + H (1)
- CS2 + hn . CS + S
- DOS + hn . CO + S
- SF6 + hn . products
- NaOH + hn . Na + OH
- NaCl + hn . Na + Cl
Jörm Burkert

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2. Staatsangehörigkeit: deutsch
3. Alter: 30 Jahre
4. Geburtsort: Bremen
5. Eltern: Eckhard Burkert und Karla Burkert (geb. Gießmann)

PROMOTION

1999 - 2003 Wissenschaftlicher Mitarbeiter der Universität Bremen
Titel der Promotion: „Modellierung der troposphärischen Ozon- und Radikalchemie“

WEITERE BERUFTÄTIGKEITEN

seit 02/ 2002 Beauftragter für Chemische Sicherheit

seit 10/ 2001 Beauftragter für Abwasserentsorgung
seit 04/ 1997 Beauftragter für das Gefahrstoffkataster

HOCHSCHULSTUDIUM

1991 - 1999 Physik an der Universität Bremen
Abschluss: Diplom (Note: 1,7)

6. Titel der Diplomarbeit: „Analyse der Rolle der Peroxyradikale in der Ozonbilanz der Atmosphäre“ (Note: 1,1)
7. Studienschwerpunkte: Umweltphysik/-chemie, Technology Assessment

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05/ 1996 - 11/ 1999 Studentische Hilfskraft am Institut für Umweltphysik
(Universität Bremen)

06/ 1996 - 10/ 1999 Dozent am Aus- und Fortbildungszentrum in Bremen für Computeranwendungen (Microsoft Applikationen)

PRAKTIKA

06/ 2001 Meteorological Institute (University of Maryland, USA)

07/ 1997 Sommerschule (Riom, Frankreich)
02/ 1996 Meteorological Service of New Zealand

03/ 1996 - 04/ 1996 National Institute for Water and Atmosphere (NIWA), New Zealand
TEILNAHME AN NATIONALEN UND INTERNATIONALEN KAMPAGNEN

FIELDVOC94, EU-Projekt, 1994-1996
BROK, Umweltministerium Bremen, 1996-1999
OPTIBA, Umweltministerium Bremen, 1997-1998
ALBATROSS, Deutsche Forschungsgemeinschaft (DFG), 1996
PRICE2, EU-Projekt, 1998-2000
PRIME, EU-Projekt, 1999-2001
INDOEX, International cooperation, 1999-2002

SCHULAUSBILDUNG

19.06.1991: Abitur, Note 1,9
1984-1991: Gymnasium in Bremen
1982-1984: Orientierungsstufe in Bremen
1978-1982: Grundschule in Bremen

SPRACHKENNTNISSE

Deutsch (Muttersprache), Englisch (fließend in Wort und Schrift), Französisch (Grundkenntnisse)

HOBBYS

Handball, Surfen, Skifahren, Rollenspiele, Lesen

ERSATZDIENST

1991-1998 Arbeiter Samariter Bund

COMPUTERKENNTNISSE

Sprachen:
Turbo Pascal, Fortran, Visual Basic
Windows Applikationen:
Word, Excel, Powerpoint, Origin, Corel Draw, etc.
Unix Applikationen:
IDL, Ghostview, etc.
VERÖFFENTLICHUNGEN


