Doctoral Thesis

Nitrogen oxides and ozone measurements at the tropopause and attributions to convection and lightning

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NITROGEN OXIDES AND OZONE MEASUREMENTS
AT THE TROPOPAUSE AND
ATTRIBUTIONS TO CONVECTION AND LIGHTNING

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NO\(_x\) (NO and NO\(_2\)) and ozone mixing ratios were measured on 98 flights during August to November 1997 in the framework of the projects POLINAT 2 (Pollution in the North Atlantic Flight Corridor) and SONEX (SASS Ozone and Nitrogen EXperiment). The fully automated measurement system NOXAR (Nitrogen Oxides and Ozone along Air Routes) was permanently installed aboard an in-service Swissair B-747 airliner operating in the North Atlantic Flight Corridor (NAFC).

A striking feature of the upper tropospheric NO\(_x\) field is the occurrence of large-scale NO\(_x\) enhancements (broad plumes) up to 3000 parts per trillion by volume (pptv). In several case studies the origin of such plumes was investigated using back trajectories, satellite infrared images and lightning observations from the U.S. National Lightning Detection Network (NLDN) and the Optical Transient Detector (OTD) satellite instrument. In the case of frontal activity above the continental U.S., the location of NO\(_x\) plumes is explained by means of maps of convective influence. In another case NO\(_x\) seems to have been produced by lightning in a marine thunderstorm over the eastern Atlantic.

Lightning activity is often triggered over the warm Gulf Stream, which is found to be an important source for the regional upper tropospheric NO\(_x\) budget, at least for the time period considered. With a method called “lightning tracing” it was shown for the first time that (in some cases) the number of lightning flashes, accumulated along back trajectories, is proportional to the NO\(_x\) concentrations observed several hundred kilometers downwind of the anvil outflows. Correlations were also observed on several other cases, which provides evidence that the frequently observed NO\(_x\) plumes are predominately caused by lightning discharges. If this view holds, the NO\(_x\) budget (immediately below the tropopause) would be largely dominated by the lightning source in the aftermath of thunderstorms. However, a conclusive answer is only possible with simultaneous measurements of tracers of planetary boundary layer pollution. Alternatively, the number of lightning flashes can be viewed as a proxy for the strength of updrafts and thus vertical transport of pollution from the planetary boundary layer. At least for thunderstorms occurring over clean marine air this second possibility can be precluded providing a model for discrimination of the two NO\(_x\) sources.

From the fact that NO\(_x\)-lightning correlations could even be observed hours to days after convective impact, it is concluded that mixing processes in active thunderstorms rapidly reduce the initially highly heterogeneous NO\(_x\) field but that following this phase, the structure of large scale plumes remains stable over relatively long periods of
time (as they decay). Understanding about upper tropospheric mixing processes could eventually be improved by investigating the decay of fine scale structure in plumes with different ages.

A climatology of air masses rising slowly from the boundary layer to cruising altitude of the B-747 has been established. The analysis suggests that the speed at which vertical transport takes place is critical for the fate of NO$_x$ molecules contained in ascending air masses. In contrast to rapid ascent during convection (which typically results in broad NO$_x$ plumes), NO$_x$ mixing ratios in slowly ascending air masses were generally lower than within air masses without a history of prior ascent. It is suggested that these low NO$_x$ concentrations are caused by washout processes (via the formation of nitric acid) taking place in the cloud systems accompanying ascending air masses.
ZUSAMMENFASSUNG

Während der Monate August bis November 1997 wurden im Rahmen der Projekte POLINAT 2 (Pollution in the North Atlantic Flight Corridor) und NASA SONEX (SASS Ozone and Nitrogen Experiment) auf 98 Flügen Stickoxid- (NO$_x$=NO+NO$_2$) und Ozon-Konzentrationen gemessen. Das vollautomatische Messsystem NOXAR war in einem B-747 Linienflugzeug der Swissair installiert. Das Flugzeug wurde während dieser Zeit hauptsächlich auf der Nordatlantik-Route eingesetzt.

Das NO$_x$ Feld in der oberen Troposphäre ist gekennzeichnet durch grossskalige Erhöhungen der NO$_x$-Konzentration bis zu 3000 pptv (broad-plumes). Diese NO$_x$- „broad plumes“ erstreckten sich über einige hundert Kilometer. In mehreren Fallstudien wurden die Bildungsmechanismen solch grosser NO$_x$-Konzentrationen untersucht, und zwar mit Hilfe von Rückwärts-Trajektorien, Infrarotbildern von Satelliten, Beobachtungen der Blitzaktivität durch das US-National Lightning Detection Network (NLDN) und mit Hilfe von Informationen des satellitengestützten Instrumentes OTD.

Mit eigens für SONEX entwickelten Karten zur Darstellung der Verteilung von konvektiv beeinflussten Luftmassen, konnte die geografische Lage von NO$_x$- „broad plumes“ für eine Reihe von untersuchten Flügen erklärt werden. In einem weiteren Fall scheint NO$_x$ durch Blitzaktivität in einem marinen Gewitter über dem östlichen Atlantik entstanden zu sein.

Gewitter werden oft über dem warmen Golfstrom ausgelöst, was sich als wichtige Quelle für die regionale NO$_x$- Bilanz in der oberen Troposphäre herausstellte, zumindest in der untersuchten Zeitspanne. Mit einer neu entwickelten Methode, genannt „lightning tracing“, konnte zum ersten Mal gezeigt werden, dass die beobachteten NO$_x$-Konzentrationen in gewissen Fällen proportional zur Anzahl der Blitze - summiert über die Rückwärts-trajektorien – ist. Die dazugehörigen NO$_x$-Konzentrationen wurden mehrere hundert Kilometer im Lee von Gewitterzonen gemessen. Das Auftreten einer derartigen Korrelation ist ein starker Hinweis darauf, dass die häufig beobachteten „broad plumes“ tatsächlich auf die Blitze zurückzuführen sind. Wenn diese Interpretation stimmt, wäre die NO$_x$-Bilanz unmittelbar unterhalb der Tropopause weitgehend durch Blitzaktivitäten aus Gewitterzonen bestimmt. Zur eindeutigen Beantwortung dieser Frage müssten jedoch gleichzeitig Indikatoren für Verschmutzungen aus der planetaren Grenzschicht gemessen werden. Andererseits kann die Anzahl der Blitze als Indikator für die Intensität des Vertikaltransportes angesehen werden, durch welchen Luftverschmutzung aus der planetaren Grenzschicht auf Reiseflughöhe gehoben werden kann. Zumindest für Gewitteraktivitäten über sauberer Meerluft kann diese zweite NO$_x$-Quelle aber ausgeschlossen werden.
Aus der Tatsache, dass die Korrelation zwischen NO\textsubscript{x} und Blitzaktivität sogar Stunden oder Tage nach konvektiven Ereignissen beobachtet werden kann, folgt, dass Mischprozesse aktiver Gewitterzellen die anfänglich sehr heterogene Verteilung von NO\textsubscript{x} rasch verkleinern, dass aber nach dieser Phase die Struktur ausgedehnter NO\textsubscript{x}-Ansammlungen während relativ langer Zeit stabil bleibt (während NO\textsubscript{x} gleichzeitig chemisch zerfällt). Analysen der Feinstruktur solcher NO\textsubscript{x}-Ansammlungen und ihrer Verminderung über die Zeit könnten das Verständnis für Mischprozesse in der oberen Troposphäre verbessern.

Es wurde eine Klimatologie von Luftmassen, die langsam von der planetaren Grenzschicht bis auf Flughöhe der B-747 ansteigen, erarbeitet. Aus der Analyse lässt sich folgern, dass die vertikale Geschwindigkeit entscheidend für das Schicksal der in den Luftmassen enthaltenen NO\textsubscript{x}-Moleküle ist. Im Unterschied zur Konvektion (welche häufig broad-plumes auf Reiseflughöhe hinterlässt) enthielten langsam aufgestiegene Luftmassen tiefere Konzentrationen als Luftmassen ohne Aufstieg. Dies legt den Schluss nahe, dass die tiefen NO\textsubscript{x}-Konzentrationen eine Konsequenz von in den Wolken stattfindenden Auswaschprozessen (via die Bildung von Salpetersäure) sind.
# CONTENTS

1 INTRODUCTION.................................................................................................................. 1

2 OZONE AND NITROGEN OXIDES IN THE TROPOPAUSE REGION................................. 5

2.1 CHEMISTRY IN THE FREE TROPOSPHERE ................................................................... 5

2.1.1 Production of Ozone................................................................................................. 5

2.1.2 Chemistry of HO\textsubscript{x} and NO\textsubscript{x}......................................................... 7

2.1.3 Response of O\textsubscript{3} to NO\textsubscript{x} increases in the UT.................................. 10

2.2 VERTICAL MOTION IN THE ATMOSPHERE.................................................................. 11

2.2.1 Motion constrained to lower levels.......................................................................... 11

2.2.2 High reaching vertical motion................................................................................. 13

1.3 TROPOSPHERIC SOURCES OF NO\textsubscript{x}................................................................ 15

1.3.1 Global NO\textsubscript{x} sources .................................................................................. 15

1.3.2 NO\textsubscript{x} production by lightning...................................................................... 16

3 NOXAR MEASUREMENT SYSTEM.................................................................................... 21

3.1 OVERVIEW..................................................................................................................... 21

3.2 GAS-FLOW .................................................................................................................... 22

1.3 CONTROL AND DATA ACQUISITION SYSTEM......................................................... 24

1.4 SYSTEM SECURITY ..................................................................................................... 24

1.5 OZONE ANALYZER ...................................................................................................... 25

1.6 NO ANALYZER............................................................................................................. 26

1.6.1 Theoretical background......................................................................................... 26

1.1.2 Measurement and calibration modes of the TRs..................................................... 28

1.1.3 Zeroing calibration................................................................................................. 29

1.1.4 Sensitivity (span) calibration .............................................................................. 30

1.1.5 Calculating the NO mixing ratio ......................................................................... 31

1.7 PHOTOLYTIC NO\textsubscript{x}/NO\textsubscript{y} CONVERTER...................................................... 31

4 MODIFICATIONS FOR POLINAT 2 & DATA QUALITY.................................................... 33

1.1 MODIFICATIONS: OVERVIEW.................................................................................. 33

1.2 OZONE MEASUREMENT ............................................................................................. 33

1.2.1 Comparison with Payrene ozone sondes ............................................................... 33

1.2.2 Laboratory studies and modifications .................................................................. 36

1.3 NO\textsubscript{x} MEASUREMENT ......................................................................................... 37

1.3.1 Zeroline: Laboratory measurements.................................................................... 37

1.3.2 New zero calibration type ................................................................................... 40

1.3.3 Zeroline: Performance in the field....................................................................... 42

1.4 DATA QUALITY ASSESSMENT .................................................................................... 44

1.4.1 Ozone Measurement.............................................................................................. 44

1.4.2 NO Measurement.................................................................................................... 45
1 Introduction

Tropospheric ozone is a potent greenhouse gas, and its radiative forcing efficiency is strongest near the tropopause [Fishman et al., 1979; Lacis et al., 1990, Johnson et al., 1992] where commercial airliners operate. Changes in the ozone abundance near the tropopause as an indirect consequence of aircraft operations is expected to enhance the radiative forcing of the atmosphere and impact climate [Hauglustaine et al., 1994; Grewe et al., 1999].

In contrast to relatively well quantified radiative forcing caused by increasing concentrations of long lived gases such as carbon monoxide, methane etc., the uncertainties associated with increasing tropospheric ozone concentrations are much larger as has been pointed out by the Intergovernmental Panel on Climate Change (IPCC) [IPCC, 1994]. This has several reasons: Ozone near the tropopause has various sources: Vast amounts can be transported down from the stratosphere in so called stratosphere-to-troposphere exchanges. Other complex dynamical processes cause large day-to-day variations of the tropopause altitude and thus changes in the ozone concentration at cruising altitude. At the tropopause itself and throughout the troposphere in general, ozone, a secondary air pollutant, is formed by a sequence of chemical reactions in a highly non-linear photochemistry from its precursor substances nitrogen oxides (NOx), carbon monoxide (CO) and hydrocarbons. Complex computer models incorporating transport of ozone as well as photochemical formation are therefore the only way to assess ozone changes [Brasseur et al., 1996] resulting from alterations of the NOx field (caused for instance by an increasing number of aircraft operations). However, the results of such models critically depend on NOx background concentration [Ehhalt et al., 1992; Schumann, 1997; Wennberg et al., 1998] with which the models are initialized. These NOx fields are highly variable both in space and time due to a number of NOx sources for which it is very difficult to achieve trustworthy quantitative estimates because they are intrinsically linked to meteorological processes, which are not yet fully understood or difficult to simulate. These sources include the in-situ production from lightning discharges [von Liebig, 1827; Zeldovich and Raizer, 1967; Goldenbaum and Dickerson, 1993], fast vertical transport of air from the polluted planetary boundary layer [Chatfield and Crutzen, 1984; Dickerson et al., 1987] and downward transport from the stratosphere where NOx is produced by photolytic decomposition of N2O. Since spaceborne measurements of NOx are not (yet) possible, in-situ measurements of the NOx field are therefore an integral and important contribution of the current debate on ozone induced radiative forcing.
Until recently, the NOx concentrations at cruising altitude had only been determined experimentally during a few episodic campaigns using dedicated research aircraft. The availability of NOx measurements has been dramatically increased by the Ph.D. thesis of Dominik Branner (ETH Zürich, Switzerland) who conducted the first systematic NOx measurements from an in-service Swissair B-747 in the period of May 1995 to May 1996 in the project NOXAR (Nitrogen Oxides and Ozone along Air Routes), with a system developed in cooperation with ECO PHYSICS AG, Dürnten, Switzerland. These automatic measurements took place between Zurich, Switzerland, and routes to Far East destinations and across the North Atlantic, leading to a tenfold increase of the globally available data of simultaneously measured NOx (NO and NO2) and ozone concentrations at these altitudes. The NOXAR measurements showed three main features of the NOx distribution [Brunner et al., 1998; Dias-Lalcaca et al., 1998; Jeker et al., 1998]:

1. Elevated NOx concentrations up to a few ppbv (parts per billion by volume) were observed during fractions of a second to several seconds. They were attributed to the crossing of freshly emitted exhaust plumes of other aircraft as was noted by Schlager et al. [1997].

2. High NOx concentrations were observed over extended areas (up to many hundred kilometers) which Brunner et al. [1998] attributed to the transport of polluted boundary layer air and to lightning emissions.

3. In summer, large scale NOx plumes were observed downwind of areas, which had been convectively active two days prior to the measurements. More recent events are rarely encountered because pilots avoid active thunderstorms. During other seasons, NOx plumes were observed predominantly downwind of frontal systems.

More detailed investigation of the origin of the (surprisingly) large number of plumes is the main aim of the present thesis. The NOx and ozone measurements performed during the first part of this thesis and which provide the basis for the analysis, were jointly performed with the coordinated European and American programs POLINAT 2 (Pollution in the North Atlantic) and NASA SONEX (SASS Ozone and Nitrogen Experiment). These campaigns were performed in autumn 1997 in the North Atlantic Flight Corridor (NAFC) and constitute the most recent efforts for getting a better understanding of the impact of aircraft emissions [Schumann et al., in press; Singh et al., 1999; Thompson et al., 1999]. While the DLR Falcon and the NASA DC-8 performed high precision measurements of a large spectrum of chemical parameters, the NOXAR system aboard the Swissair B-747 systematically measured the distribution of nitrogen oxides (NO and NO2) and ozone during 98 traverses of the North Atlantic in the period of August 13 to November 23, 1997 [Jeker et al., 1998]. After extensive raw-data processing the data were converted into the Hippskind-Gaines format and archived at DLR and NASA.
Ames to provide a “climatological” overview of NOx and ozone during these campaigns.

Thereafter, research mainly focused on the foremost uncertainty of the lightning contribution to the total NOx abundance, which according to the latest IPCC report is a key factor in understanding the NOx budget at the tropopause [IPCC, 1999]. A technique called “lightning tracing” was developed and for the first time allowed to correlate NO concentrations measured along the flight track to the number of lightning flashes accumulated along back trajectories starting inside high NO concentrations.

After a short description of the relevant chemical and physical processes in the tropopause region (chapter 2), the thesis is structured into three main parts:

- **Measurements:** In chapter 3 and 4 the NOXAR system is described as well as laboratory experiments leading to several modifications of the system.
- **Data Quality and Availability:** In chapters 4 and 5 obtained data quality is assessed and results of an intercomparison flight performed with the DLR Falcon aircraft is reported. Data availability is presented in the chapter 5.
- **Tracing lightning influence:** The aforementioned tools for getting semi-quantitative source estimates are introduced in chapter 6. In chapter 7 accuracy is demonstrated and discussed in a number of selected case studies, which highlight the major impact that lightning accompanied convection exhibits on the upper tropospheric NOx budget.

Results are then tentatively extrapolated to the global scale by “correlating” observations from the OTD lightning detection satellite to NOXAR broad-plumes (chapter 8). In chapter 9 conclusions are drawn and future research is suggested.
2 Ozone and Nitrogen oxides in the Tropopause region

This chapter aims at illustrating chemical and physical processes determining NO\textsubscript{x} and ozone abundances at commercial airliner's cruising altitude. The first section focuses on the chemical reactions responsible for the production and destruction of ozone. As will be shown the chemical reaction system at these altitudes crucially depends on the availability of the chemical "key players" HO\textsubscript{x} and NO\textsubscript{x}. Sources and sinks of the latter molecules are numerous and variability throughout the atmosphere very large which is also a consequence of a number of different meteorological processes. This widens the discussion to important dynamical processes such as frontal systems and thunderstorms, which will be accomplished in the following section on cloud venting. The last section is devoted to the discussion of tropospheric NO\textsubscript{x} sources and includes a discussion of lightning NO\textsubscript{x} production.

2.1 Chemistry in the free Troposphere

2.1.1 Production of Ozone

Chemical reactions governing ozone production near the tropopause, where commercial aircraft cruise, differ significantly from stratospheric ozone formation mechanisms. Stratospheric ozone is produced from the photolytic decomposition of oxygen by energy absorption from solar UV radiation below 242 nm [Chapman, 1930]. The hereby formed ozone layer as well as oxygen molecules screen out radiation with wavelengths shorter than 300 nm so that these wavelengths are not available for chemical reactions at lower levels, such as the tropopause region. There ozone (O\textsubscript{3}) is produced in a sequence of reactions following the oxidation of reduced species such as carbon monoxide (CO) [Crutzen, 1973] and (to a lesser extent) methane (CH\textsubscript{4}).

\[
\begin{align*}
\text{CO} + \text{OH} & \rightarrow \text{H} + \text{CO}_2 \quad \text{(R2.1)} \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} \quad \text{(R2.2)} \\
\text{HO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{OH} \quad \text{(R2.3)} \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \quad \text{(R2.4)} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} \quad \text{(R2.5)}
\end{align*}
\]

In the presence of a third body (M) such as N\textsubscript{2} the free hydrogen atom (R2.2) rapidly combines with oxygen to form a hydroperoxy-radical (HO\textsubscript{2}). The latter oxidizes nitric oxide (NO) to nitrogen dioxide (NO\textsubscript{2}) and this reaction represents the rate limiting step in ozone production at cruising altitude [Jaeglé et al., 1999a]. The OH to HO\textsubscript{2} ratio is
Ozone and nitrogen oxides in the tropopause region

determined primarily by reactions (R2.1)-(R2.3) and thus by the NO/CO ratio, if the NO mixing ratio exceeds 10 pptv [Fishman and Crutzen, 1978]. NO\textsubscript{2} is photolyzed in the presence of sunlight (hv), and leads to the formation of NO and a free O atom (R2.4). In combination with an O\textsubscript{2} molecule, ozone (O\textsubscript{3}) is formed through reaction (R2.5). The sequence of reactions triggered by the oxidation of carbon monoxide thus leads to the formation of one O\textsubscript{3} molecule per oxidized CO molecule (R2.6). Note that in this reaction system neither NO\textsubscript{x} (=NO+NO\textsubscript{2}) nor HO\textsubscript{x} (=HO+HO\textsubscript{2}) molecules are consumed so that they catalyze the oxidation:

\textbf{net: } CO+2O\textsubscript{2} \rightarrow CO\textsubscript{2}+O\textsubscript{3} \hspace{1cm} (R2.6)

The more abundant methane molecule (about 1.7 ppmv as opposed to 0.05-0.2 ppmv CO) also leads to ozone formation but is less important due to a slower initiation reaction (R2.7) and a longer reaction path.

\begin{align*}
\text{CH}_3+\text{OH} & \rightarrow \text{CH}_3+\text{H}_2\text{O} \hspace{1cm} (R2.7) \\
\text{CH}_3+\text{O}_2+\text{M} & \rightarrow \text{CH}_3\text{O}_2+\text{M} \hspace{1cm} (R2.8) \\
\text{CH}_3\text{O}_2+\text{NO} & \rightarrow \text{CH}_3\text{O}+\text{NO}_2 \hspace{1cm} (R2.9) \\
\text{CH}_3\text{O}+\text{O}_2 & \rightarrow \text{HCHO}+\text{HO}_2 \hspace{1cm} (R2.10)
\end{align*}

The first step (R2.7) of the methane oxidation chain leads to one CH\textsubscript{3} radical which quickly pairs with oxygen in the presence of a third body to form a methylperoxy radical (CH\textsubscript{3}O\textsubscript{2}) (R2.8). CH\textsubscript{3}O\textsubscript{2} oxidizes nitric oxide to NO\textsubscript{2} in a reaction where a methyloxy radical (CH\textsubscript{3}O) is produced (R2.9). The latter combines with oxygen and forms formaldehyde (HCHO) and a hydroperoxy radical (HO\textsubscript{2}) in reaction (R2.10). HO\textsubscript{2} subsequently reacts with NO (R2.3) which reforms and thus closes the reaction chain initiated by the oxidation of methane and ultimately leads to the production of two ozone molecules (R2.4-R2.5).

Formaldehyde photolyzes to CO in reactions (R2.11) to (R2.13) and oxidation of the latter molecule results in an additional ozone molecule and in one HO\textsubscript{2} radical following reactions (R2.1) through (R2.5).

\begin{align*}
\text{HCHO} + \text{hv} & \rightarrow \text{H}+\text{HCO} \hspace{1cm} (R2.11) \\
\text{H}+\text{O}_2+\text{M} & \rightarrow \text{HO}_2 \hspace{1cm} (R2.12) \\
\text{HCO}+\text{O}_2 & \rightarrow \text{HO}_2+\text{CO} \hspace{1cm} (R2.13)
\end{align*}

Both the oxidation of CO and to a lesser extent that of CH\textsubscript{3} therefore lead to a net gain in ozone. The dominance of the CO- over the CH\textsubscript{4}-path is a consequence of the slower
reaction of CH₄ with the OH radical which can neither be compensated by the larger abundance nor by the higher ozone yield per methane molecule. Higher hydrocarbons lead to similar but more complex reaction sequences that CH₄ oxidation.

The rates of both the CO and the CH₄ oxidation sequence (and thus ozone formation) depend directly on the availability of HOₓ (=HO+HO₂) and NOₓ (=NO+NO₂) due to the low background concentrations of the latter molecules in the upper troposphere (UT). Availability of these molecules is determined by chemical reactions and physical processes which are summarized in section 2.1.2 and , respectively.

2.1.2 Chemistry of HOₓ and NOₓ

2.1.2.1 Sources of HOₓ

The photolysis of ozone (at hv<315nm) is the most important primary source of the OH radical.

\[
\begin{align*}
\text{O}_3 + \text{sunlight} & \rightarrow \text{O}(^1\text{D}) + \text{O}_2 \\
\text{O}(^1\text{D}) + \text{H}_2\text{O} & \rightarrow 2\text{OH}
\end{align*}
\]

Other sources of OH and HO₂ include the photolysis of acetone [Singh et al., 1995; Arnold et al., 1997], peroxides [Chatfield and Crutzen, 1984], and formaldehyde (R2.12). Moreover, Wennberg et al. [1998] noted that measured HOₓ concentrations on a number of recent NASA campaigns were larger than what had been anticipated from models constrained with measured CO and CH₄ concentrations. It was concluded that the photolysis of carbonyl and peroxide compounds might provide the required source to sustain the measured HOₓ abundances. During the SONEX mission primary sources of HOₓ (=OH + HO₂ + 2H₂O + 2CH₃OOH + HNO₂ + HNO₄) from ozone photolysis (R2.14 and R2.15) and acetone photolysis were of comparable magnitude [Jaeglé, et al., 1999b].

2.1.2.2 Sinks of HOₓ and NOₓ

HOₓ is removed from the atmosphere by a number of processes, typically leading to H₂O on time scales of 5-30 minutes [IPCC, 1999]. A simple reaction of this type is the combination of a hydroxy with a hydroperoxy radical to water and oxygen.

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

Formation of the easily soluble nitric acid (HNO₃) molecule is the most important sink for NOₓ. Two different reaction paths exist; the first also removes OH radicals (R2.17).
OH+NO\textsubscript{2}+M → HNO\textsubscript{3}+M \hspace{1cm} (R2.17)

The second path (R2.18 – R2.20) only gains importance at night, when appreciable NO\textsubscript{2} concentrations prevail at cruising altitude due to the absence of the photolysis reaction (R2.4). In a slow reaction between NO\textsubscript{2} and O\textsubscript{3} the highly reactive NO\textsubscript{3} radical is formed (R2.18). Thereafter an equilibrium with di-nitrogen pentoxide (N\textsubscript{2}O\textsubscript{5}) is rapidly achieved through reaction (R2.19). Finally, hydrolysis on sulfate aerosols leads to the production of HNO\textsubscript{3} (R2.20). According to Jaeglé et al. [1998] this second HNO\textsubscript{3} generation path contributed about 10-30 % of NO\textsubscript{x} loss during the NASA SUCCESS mission.

\[
\begin{align*}
\text{NO}_3^+ + \text{O}_3 & \rightarrow \text{NO}_3^+ + \text{O}_2 \hspace{1cm} (R2.18) \\
\text{NO}_2 + \text{NO}_3 & \leftrightarrow \text{N}_2\text{O}_5 \hspace{1cm} (R2.19) \\
\text{N}_2\text{O}_5 + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3 \hspace{1cm} (R2.20)
\end{align*}
\]

Jaeglé et al. [1998] compared measurements from the SUCCESS campaign to model results and could find no evidence of heterogeneous recycling of NO\textsubscript{x} from HNO\textsubscript{3}, on aerosol surfaces which is in contrast to previous work [Dentener and Crutzen, 1993]. If this new finding holds, the conversion of NO\textsubscript{x} to HNO\textsubscript{3} followed by reaction (R2.21) therefore constitutes a final exit of NO\textsubscript{x} from the atmosphere and thus determines the NO\textsubscript{x} lifetime.

\[
\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3 \hspace{1cm} (R2.21)
\]

Permitric acid (HNO\textsubscript{4}) and NO\textsubscript{2} catalyze reactions, which provide an irreversible, sink for two HO\textsubscript{x} molecules (R2.22 and R2.23).

\[
\begin{align*}
\text{HO}_2 + \text{NO}_2 + \text{M} & \rightarrow \text{HNO}_4 + \text{M} \hspace{1cm} (R2.22) \\
\text{OH} + \text{HNO}_4 & \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2 \hspace{1cm} (R2.23)
\end{align*}
\]

Last but not least, in the absence of light, water-superoxide is formed from two hydroxy radicals. Note that this reaction is reversed through light absorption.

\[
\text{2HO}_2 + \text{M} \leftrightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{M} \hspace{1cm} (R2.24)
\]

During SONEX reaction (R2.16) was the dominant sink for HO\textsubscript{3} for NO\textsubscript{x}<50 pptv and for larger concentrations (R2.23) dominated [Jaeglé et al., 1999b].
2.1.2.3 NO\textsubscript{x} partitioning and lifetime at cruising altitude

During daytime on the ground, NO\textsubscript{x} partitioning between NO\textsubscript{2} and NO is primarily determined by the photolysis of NO\textsubscript{2} (R2.4) and the reaction between NO and O\textsubscript{3} (R2.25) on the side of NO\textsubscript{2}. For constant ozone concentrations partitioning changes in favor of NO with increasing altitude due to the strongly temperature dependent NO\textsubscript{2} formation reaction rate $k_{25}$ of (R2.25).

\[
O_3 + NO \rightarrow NO_2 + O_2 \quad \text{(R2.25)}
\]

with $k_{25} = 2 \cdot 10^{-12} \cdot \exp(-1400/T) \left[ \text{cm}^3/(\text{# molecules})^{-1} \cdot \text{s}^{-1} \right]$

The left panel in Figure 2.1 shows the decrease of $k_{25}$ as a function of altitude. During daytime, the photolysis of NO\textsubscript{2} (R2.4) dominates so that NO constitutes the main share (about 90\%) of NO\textsubscript{x} at typical temperatures and ozone concentrations in the upper troposphere.

The lifetime of NO\textsubscript{x} against conversion to HNO\textsubscript{3} (R2.17) depends on the NO\textsubscript{2}/NO ratio because NO\textsubscript{2} is the reactant species for the conversion.

The right panel in Figure 2.1 illustrates how the NO\textsubscript{x} lifetime increases from about 1 day at 2 km to 8 days at 11 km, in large part because of the temperature dependence of the reaction rate $k_{25}$ and the resulting partitioning of NO at the higher altitudes [Jaeglé et al., 1998].

The lifetime of NO\textsubscript{x} determines the number of cycles during which NO\textsubscript{x} catalytically produces ozone. In the troposphere the ozone production efficiency per released NO\textsubscript{x}...
molecule therefore increases with altitude. The NO$_x$ lifetime also increases with stronger photolysis (e.g. in summer) of NO$_2$ which both reduces removal rates via HNO$_3$ and also yields a free O radical which thus increases ozone production.

2.1.3 Response of O$_3$ to NO$_x$ increases in the UT

The previous sections highlighted that NO$_x$ and HO$_x$ are linked by a number of important reactions; the concentration of each depends on the concentration of the other. These complex interactions between individual components lead to a non-linear dependence of ozone production on the level of NO$_x$ [Liu et al., 1987]. Numerical computer models are therefore an attractive way to assess the impact that perturbations of the NO$_x$ field have on ozone concentrations. In general such model calculations predict that ozone production should increase with increasing NO$_x$ concentrations up to a threshold NO$_x$ value of a few hundred pptv (NO$_x$ limited regime), beyond which further increases in NO$_x$ result in a decrease in ozone production [Brasseur et al., 1996]. In the context of the upper troposphere, the latter is referred to as the NO$_x$-saturated regime (it is commonly known as the hydrocarbon-limited regime in the lower troposphere). Figure 2.2 shows the calculated net production of ozone at approximately 10 km as a function of the NO$_x$ abundance [Brasseur et al., 1996].

![Figure 2.2](image)

**Figure 2.2.** Net ozone production rate in cubic centimeters per second calculated as a function of the atmospheric NO$_x$ mixing ratio (in parts per billion by volume) at 50°N at 10-km altitude in July for clear sky conditions. Adapted courtesy Guy Brasseur, NCAR.

Curve A represents model calculations by Ehhalt et al. [1992] who adopted mixing ratios of 84 ppbv for ozone, 73 ppbv for carbon monoxide, 1.6 ppmv for methane, and 50 ppmv for water vapor. In addition, the effect of non-methane hydrocarbons is
neglected, and the solar diurnal cycle is ignored. The calculated production of ozone \( P(O_3) \) is substantially modified when the mixing ratio of water vapor is doubled (100 ppmv; curve B), when, in addition, the effects of hydrocarbons (i.e. methane) are taken into account (curve C), and finally when the diurnal cycle is included in the model calculation (curve D). It is therefore not possible to indicate a single \( \text{NO}_x \) threshold volume-mixing ratio, at which the regime changes from \( \text{NO}_x \) limited to \( \text{NO}_x \) saturated. Jaeglé et al. [1999a] noted that this type of graph can easily be misinterpreted since convective events not only increase \( \text{NO}_x \) at cruising altitude but often also enhance \( \text{HO}_x \) precursors which thus leads to shifting of the \( O_3 \) production curve. The observed correlation between elevated \( \text{NO}_x \) and \( \text{HO}_x \) sources resulted in a positive relationship between \( P(O_3) \) and \( \text{NO}_x \), extending over the full range of \( \text{NO}_x \) concentrations observed during SONEX (up to 1000 pptv). By filtering out this association Jaeglé et al. [1999a] observed that ozone production in fact approached \( \text{NO}_x \)-saturated conditions for \( \text{NO}_x \) concentrations larger than 80 pptv. This result suggests for solar intensity typical for autumn little sensitivity of \( P(O_3) \) to future increases in \( \text{NO}_x \) emissions from aircraft (which, unlike convective injection are not associated with a large source of \( \text{HO}_x \)).

### 2.2 Vertical motion in the atmosphere

In this section mechanisms for vertical transport are briefly outlined as far as important in the context of this study. Other dynamical processes (such as cyclogenesis) are directly discussed and applied to NOXAR measurements in chapters 5 to 8.

Vertical transport in the atmosphere can occur on a large variety of temporal and spatial scales. An excellent overview on that topic is given in the review article on cloud venting by Cotton et al. [1995]. Of all types of cloud venting, the following types of vertical appeared to be most important for the interpretation of the NOXAR measurements: Slowly ascending air masses (section 8.2) associated with frontal systems. Such ascending motion can be connected to the formation of precipitation. During ascent, \( \text{HNO}_3 \) is formed from \( \text{NO}_x \) (R2.17) which is subsequently washed-out. If vertical motion is very rapid such as during convection, it can be accompanied by lightning and also lift pollutants from the atmospheric boundary layer to cruising altitude. Lightning is a very important \( \text{NO}_x \) source for the upper troposphere, and is further discussed in section 2.3.

#### 2.2.1 Motion constrained to lower levels

Ordinary cumuli are not major contributors to the mixing of atmospheric boundary layer air to tropopause altitude but these clouds are discussed exemplarily to introduce a few terms and definitions used later in the text. Solar radiation heats the Earth’s surface
and is subsequently transferred to overlaying air masses. This leads to bulbs of hotter and thus less dense air (thermals), which start to rise. During ascent, these air masses cool through adiabatic expansion and their density therefore increases relative to that of ambient air. If this motion is slow enough, the air masses may also mix with ambient air, which slows down ascent. Thermals, which ascend rapidly enough, may reach the dew point. The level at which condensation first takes place is called *lifting condensation level* (LCL). Even more buoyant (less dense than ambient air) thermals ascend to the *level of free convection* (LFC). Latent heat liberated during condensation to form droplets yields enough buoyancy for the cloud to ascend into the *capping inversion*. Stull [1985] referred to such clouds as *active cumuli*.

![Figure 2.3. The left panel shows typical atmospheric soundings of dew point ($T_d$) and temperature ($T$) for conditions where fair weather clouds prevail. The upper limit of the atmospheric boundary layer (ABL) is marked with ($Z_b$). The lifting condensation is marked with (LCL) and the level of free convection with (LFC). The right panel shows locations of active and passive clouds.](image)

The capping inversion prevents most clouds from further ascending and dry air mixing of the thermal bulb leads to erosion of the cloud. This state is what Stull [1985] referred to as a *passive cloud*. Such *ordinary cumulus clouds* (are no major venters of boundary layer air, but instead tend to enhance vertical mixing in and slightly above the boundary layer, as stated, for instance by Riehl [1979].
2.2.2 High reaching vertical motion

Interactions of air from lower levels with air masses at cruising altitude mainly happen through cumulonimbus (i.e. thunderstorm) clouds or through a number of air-streams associated with extratropical cyclones.

Cumulonimbus clouds are rain producing, deep tropospheric clouds that are generally accompanied by lightning, thunder and gusty surface winds [Cotton et al., 1995]. Two parameters reasonably well define the regimes for different cumulonimbus types. One is CAPE (convective available potential energy) which provides a measure of the maximum possible kinetic energy that a statically unstable parcel can acquire (neglecting effects of water vapor and condensed water on the buoyancy), assuming that the parcel ascends without mixing with the environment and instantaneously adjusts to the local pressure [Holton, 1992]. The buoyancy \( b(z) \) is the acceleration that a parcel experiences due to the density (or temperature \( T \)) gradient with ambient air (2-1).

\[
b(z) = g \left( \frac{\rho_{\text{env}} - \rho_{\text{parcel}}}{\rho_{\text{parcel}}} \right) = g \left( \frac{T_{\text{parcel}} - T_{\text{env}}}{T_{\text{env}}} \right) \tag{2-1}
\]

where \( \rho \) is the density air parcel (\( \rho_{\text{parcel}} \)) and its surroundings (\( \rho_{\text{env}} \)), g the earth acceleration.

By integrating over altitude the maximum kinetic energy per unit mass [J/kg] that a buoyant parcel could obtain by ascending from a state of rest at the level of free convection (LFC) to the level of neutral buoyancy (i.e. same ambient density as ambient air) near the tropopause can be calculated by (2-2). This quantity is called CAPE.

\[
\text{CAPE} \equiv \frac{w_{\text{max}}^2}{2} = \int_{LFC}^{\text{top}} g \left( \frac{T_{\text{parcel}} - T_{\text{env}}}{T_{\text{env}}} \right) dz \tag{2-2}
\]

Price and Rind [1992] pointed out that if all CAPE were converted to kinetic energy of upward vertical motion, then the updraft velocity \( w \) at the equilibrium level would be

\[
w_{\text{CAPE}} = \sqrt{2(\text{CAPE})} \tag{2-3}
\]

Note that CAPE is an overestimate of the actual kinetic energy realized by a non-entraining parcel since the negative buoyancy contribution of liquid water reduces the effective buoyancy, especially in the tropics [Holton, 1992]. CAPE only describes the potentially available energy but a storm can be inhibited if strong wind shear exists between the level of free convection and the level of neutral buoyancy. The Bulk
Ozone and nitrogen oxides in the tropopause region

*Richardson Number* \((R_f)\) accounts for that effect and can be used to determine storm type (see table 2.1).

\[
R_f = \frac{\text{CAPE}}{0.5(\Delta w)^2}
\]  

(2-4)

*Cotton et al.* [1995] classified different storm types based upon CAPE and \(R_f\) values (table 2.1).

<table>
<thead>
<tr>
<th>Thunderstorm Type</th>
<th>CAPE [J/kg]</th>
<th>(R_f) [-]</th>
<th>Updraft speeds [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ordinary continental</td>
<td>&lt;2000</td>
<td>&gt;50</td>
<td>8-15</td>
</tr>
<tr>
<td>ordinary marine</td>
<td>200-500</td>
<td>&lt;6</td>
<td></td>
</tr>
<tr>
<td>intense multicellular</td>
<td>&gt;3000</td>
<td>&gt;50</td>
<td>&lt;35</td>
</tr>
<tr>
<td>supercell</td>
<td>&gt;3000</td>
<td>15-35</td>
<td>40</td>
</tr>
</tbody>
</table>

*Table 2.1. Classes of thunderstorms with empirical values published in Cotton et al.* [1985]. For marine thunderstorms see Jorgenson and Lemone, [1989] and Takahashi [1990].

It can be demonstrated that all these storm types exhibit rather different updraft speeds and that lightning frequencies are not proportional to the updraft speeds (see also 2.3.2). This topic will be further discussed in section 2.3.2 dealing with parameterizations of the lightning flash rate. However, all these storm types result in rapid vertical transport of air from the atmospheric boundary layer to the upper troposphere. If air of the boundary layer is clean (as suspected over the ocean) pollutant concentration at the tropopause can potentially decrease, also due to ascending air motion. If convection takes place over polluted urban areas, pollution can be carried to higher altitudes where \(NO_x\) lifetime is larger [Dickerson et al., 1987].

*Cotton et al.* [1995] estimated that the most significant amounts of vertical transport takes place through *extratropical cyclones*. They are the most prolific cloud-producing systems in middle and high latitudes. Their principal driving force is the poleward temperature decrease, usually concentrated in rather narrow baroclinic zones (i.e. meridional temperature gradients) or fronts. These baroclinic zones become unstable with respect to wave-like perturbations, resulting in the development of cyclones [Cotton et al., 1995]. These systems are characterized by many complex air streams. In the warm frontal region warm air slowly ascends on the colder air masses, which causes condensation and thus stratiform (i.e. large-scale) precipitation. Even if such air rises from the polluted continental boundary layer, could the slow ascent combined with the stratiform rain potentially cause a reduction in the \(NO_x\) concentration via rainout of nitric acid (R2.17). This effect is probably even larger at lower levels, where \(NO_x\) portioning is more on the side of \(NO_2\). However, along the cold front where stronger ascent occurs
and the air in the warm sector generally contains large amounts of CAPE, deep convective clouds are common. Rapidly deepening coastal cyclones are strongly affected by deep convection. During POLINAT 2 and SONEX convection was often associated with the West-East passage of frontal systems over the US east coast and thunderstorms typically intensified over the warm Gulf stream where high lightning frequencies were often observed (see section 7). Transport therefore occurs on many different levels and redistribution of NO species is also closely coupled to chemistry (i.e. lifetime). In the next section the most important sources of NO species are listed.

2.3 Tropospheric sources of NO species

2.3.1 Global NO species sources

The primary sources of NO species in the troposphere are fossil fuel combustion, biomass burning, soil emissions, lightning, transport from the stratosphere, ammonia oxidation, and aircraft exhaust [IPCC, 1999]. The largest source is fossil fuel combustion; 95% of its emissions take place in the Northern Hemisphere predominately over the continents [Lee et al., 1997]. Biomass burning occurs primarily in the continental tropics and underlies a seasonal cycle [e.g. Crutzen and Andreae, 1990; Thompson et al., 1996]. During POLINAT 2/SONEX no significant bush fires occurred which would have affected measurements over the US continent or in the North Atlantic Flight Corridor [Henry Fuelberg, Florida State University, personal communication, 1998]. (However, the B-747 was also operated on Asian routes during a few flights, and air masses downwind of the intense 1997 Indonesian Forest Fires were therefore potentially sampled with the NOXAR system.)

Soil emissions arise from microbial denitrification processes. The production rates are regionally variable and depend on numerous parameters [e.g. Williams et al., 1992]. The burning of fossil fuel consumption accounts for more than 85% of the global NO species emission-share, and is typically directly emitted into the lowest few kilometers of the atmosphere. Moreover, soil emissions and emissions from fossil fuel combustion are often confined to the atmospheric boundary layer (ABL) and occasionally fully separated from the free troposphere through the formation of an inversion layer (cf. Figure 2.3).

In the stratosphere, NO species is primarily produced from the photolytic decomposition of nitrous oxide (N₂O). N₂O is produced from numerous sources and its concentration has been increasing at a rate of 0.5-0.8 ppbv yr⁻¹ [IPCC, 1996]. As a result of this source, NO species concentrations in the LS are quite large, increasing from about 100 pptv at the tropopause to as much as 3000 pptv at an altitude of 20 km [IPCC, 1999].

Aircraft are thus the only significant source generating NO species directly at the tropopause level. These emissions are now relatively well quantified at about 0.5 teragrams of N
Ozone and nitrogen oxides in the tropopause region

per year [Baughcum et al., 1996a,b; Gardner et al., 1997]. This source is relatively small compared to the vast amounts of NO\textsubscript{x} emitted on the ground. However, most of these emissions are thought to be removed from the atmosphere by uptake on cloud droplets followed by precipitation. If this view holds, then the upper troposphere-lower stratosphere region (UT-LS), represents a relatively pristine environment that is affected episodically during weather events that rapidly lift surface air or bring down stratospheric air [Friedl, 1999]. Quantifying the share of surface emission reaching the tropopause is difficult. To complicate matters, the same weather events responsible for surface NO\textsubscript{x} transport may also be associated with lightning which can inject to these upper altitudes. Lightning discharges are known to produce vast amounts of NO\textsubscript{x} [e.g. Price and Rind, 1992; Levy et al., 1996], but their contribution to the total NO\textsubscript{x} budget is very uncertain because it is extremely difficult to measure directly [IPCC, 1999]. One of the main aims of this thesis will be to further investigate this source. Some theoretical background is given in the following section. Lightning detection networks used to interpret the measurements are described in section 6.1.3.

2.3.2 NO\textsubscript{x} production by lightning

Cloud electrification is a consequence of charge separation. In convective clouds this can happen due to precipitation and during the strong vertical updrafts. Accordingly, the two main hypothesis for charge separation are the precipitation and the convection hypothesis [cf. Price and Rind, 1992]. The precipitation hypothesis relies on a few microphysical processes for the build-up of charge in thunderstorms: charge transfer by collision between graupel and ice particles, charge transfer by induction, and charge separation due to the thermoelectric effect. The precipitation hypothesis assumes the build-up of a net dipole within a thunderstorm during the gravitational sedimentation of precipitation particles. The convection hypothesis relies on convective motions to transport externally derived positive ions into the cloud from below, where they get attached to cloud and precipitation particles [Vonnegut, 1963]. The large scale separation then results from updrafts carrying the positively charged particles to the upper portions of the cloud, while downdrafts bring negative ions from above the cloud top to the cloud base [Price and Rind, 1992]. Through charge separation an electric potential (V) is built up. In thunderstorms the breakdown potential (gradient) V for the initiation of a lightning flash is of the order of 5x10\textsuperscript{5} V/m [Berger, 1977]. Estimating the amount of NO\textsubscript{x} produced per discharge is rather difficult as the mechanism for the production is not well understood. The concept usually adopted is that from Zel’dovitch [Zel’dovitch and Raizer, 1967], by which NO is produced through high temperature dissociation of molecular nitrogen (N\textsubscript{2}) and oxygen (O\textsubscript{2}), and subse-
quent reaction with atomic species. Production involves a series of unstable species. Here only net reactions are given in reactions (R 2.26 and R 2.27).

\[
\begin{align*}
O + N_2 & \rightarrow NO + N \quad (R2.26) \\
N + O_2 & \rightarrow NO + O \quad (R2.27)
\end{align*}
\]

The emission occurs in the form of NO, and is followed by oxidation of NO to NO\textsubscript{2} by O\textsubscript{3}. However, there appear to be two schools of thought on whether NO is mainly produced by the expanding shock wave which causes instantaneous energy deposition along the flash [e.g. Chameides, 1979] or in the ohmically heated core [e.g. Bhetenabhotla et al., 1985]. NO production during the corona phase of a lightning discharge is a third possibility but a recent theoretical study suggested that it is negligible [Coppens et al., 1998].

A theoretical study by Goldenbaum and Dickerson [1993] suggested that the rate of NO production drops off rapidly with decreasing air density and thus altitude. Operational ground based lightning detection networks (see also section 6.1.3), however, only provide peak-current and location of cloud-to-ground discharges (CG) but not the desired 3D structure and dissipated energy per flash. To add to existing uncertainties, Gallardo and Cooray [1996] pointed out that the present understanding of the mechanisms for the formation of NO in electrical discharges is not sufficient to elucidate, on physical grounds, the ranking (expressed as the ratio of the frequencies f\textsubscript{CC}/f\textsubscript{IC}) between intra-cloud (IC) and CG discharges as NO producers. The ranking can vary considerably depending on storm type and might even be biased by artifacts of the observation systems [see e.g. discussion in Dye et al., submitted]. Values typically described in the literature range from 0.1 to 1.0.

By merging four years of observations from the OTD lightning detection satellite with the U.S. National Lightning Detection Network, Boccippio et al., (2000) unveiled significant spatial variability of the IC to CG ratio across the United States (see also 6.1.3). The most violent storms exhibiting ratios up to 10 were concentrated over the Great Plains region. In contrast to that IC to CG ratios of almost 1:1 were identified over the Appalachian Mountains in the East, and the Rockies and Sierra Nevada mountains in the West. There, the ground is closer to the main negative charge layer and thus less insulating air is between opposite charges so that lightning will discharge more easily. Moreover, topography may keep storms from organizing supercells.

Different NO\textsubscript{x} production rates for both discharge types (CG and IC) combined with these observed spatial gradients in the IC to CG ratios across the U.S., thus imply systematic spatial patterns of the lightning NO\textsubscript{x} production. Adopting as an example the Gallardo and Cooray [1996] theory by which IC and CG are equally strong NO\textsubscript{x} pro-
Ozone and nitrogen oxides in the tropopause region

ducers, would identify the Great Plains as an area of particularly strong lightning NO$_x$ production (assuming similar CG frequencies in both regions).

Despite rather large uncertainties, lightning NO$_x$ emissions potentially have an important share in the upper tropospheric NO$_x$ budget (ranging from 2 to 20 Tg N/y) [Lee et al., 1997]. This can be explained by the long NO$_x$ lifetime below the tropopause, where NO$_x$ is deposited following strong updrafts in thunderstorms [Pickering et al., 1998] (see also section 2.1.2.2). Therefore, even if production rates from the lower end of the uncertainty range are taken, the lightning contribution to the NO$_x$ budget at cruising altitude might be of considerable importance. This has also been pointed out in GCM (global circulation model) studies, in which variability in the upper tropospheric NO$_x$ field was significantly increased through the introduction of a lightning source [e.g. Flateau and Hov, 1997]. Levy et al. [1996] found in a modeling study that lightning played a major role in causing NO$_x$ maxima in the tropics and summertime continental midlatitudes. These findings were confirmed in a follow-up paper [Levy et al., 1999] in which similar simulations were extensively validated against available observations from surface stations and aircraft missions.

However, total NO$_x$ production in modeling studies are highly uncertain and are often scaled to satisfy a given constraint of global total NO$_x$ production such as given in Price et al. [1997]. For a validation of such results, further laboratory studies and measurement campaigns are therefore needed.

Huntrieser et al. [1998] compiled a comprehensive survey of previous studies on transport and production of NO$_x$ in electrified thunderstorms. They note that only a limited number of in-situ studies with anvil penetrations have so far been carried out, predominantly over the American continent [Frantzblau and Popp 1989; Luke et al., 1992; Ridley et al., 1996], the Pacific Ocean [Chameides et al., 1987; Ridley et al., 1987] and more recently over Germany and Switzerland in the field campaign LINOX (lightning-produced NO$_x$) [Huntrieser et al., 1998; Höller et al., 1999]. The EC sponsored EULINOX (European Lightning Nitrogen Oxides Project) programme continued these research efforts during the summer of 1998. These projects as well as the American project STERAO-A (Stratosphere-Troposphere Experiment – Radiation, Aerosols, Ozone – Part A Deep Cumulus) [Dye et al., in press] have produced very rich data sets but have shown greater need to understand the complex mechanisms and contributions of lightning-produced NO$_x$.

In chemical modeling studies the lightning production of NO$_x$ is often parameterized based on output from numerical weather models. Williams et al. [1985] first presented an empirical relationship between measured lightning frequencies and convective cloud top heights. The latter quantity is often not directly available in numerical weather models but can be estimated from other quantities such as CAPE (see expression 2-3).
The basic idea of such a concept (see also Vonnegut, 1963; Price and Rind, 1992) is that electrical power (W) of a region of space charge increases rapidly with its size. The electrical power (W) between two point charges (q and q') is given by expression (2-5)

\[ W = \frac{Kqq'}{R} \quad (2-5) \]

where \( K = \frac{1}{4\pi\varepsilon_0} \) and \( \varepsilon_0 \) is the permittivity constant.

In an electrified cloud, however, instead of point charges there are regions of positive and negative space charges (Q), therefore

\[ W = \frac{KQQ'}{R} \quad (2-6) \]

where \( Q = q \times \text{Volume} - q \times H^3 \), and \( H \) is the vertical storm dimension. Rewriting expression (2-6) with the cloud top height therefore suggests that the power \( W \) of an electrified convective cloud is proportional to the \textit{fifth power} of the vertical storm dimension \( H \) (since \( H \sim R \)). Greater charge build-up can result in more rapid achievement of the breakdown potential, which then leads to more frequent lightning discharges. This fifth power law is in agreement with the empirical relationship brought forward by Williams [1985]. However, Price and Rind [1992] noted that the relationship is only valid for continental but does not hold for marine thunderstorms, which typically exhibit smaller updraft velocities and thus low values of both CAPE and lightning frequencies [Williams et al., 1990]. Price and Rind [1992] therefore introduced an additional parameterization for marine thunderstorms. However, several studies demonstrated that agreement with observations of this marine formulation is rather poor. Michalon et al. [1999] pointed out that the droplet concentration is a key parameter for cloud microphysical properties and must be added to "classical" parameters (CAPE, cloud-top height and others) which previously had been used for parametrizing lightning frequencies. Since droplet concentrations are typically not predicted by GCMs and further show great variability, two different "standard" droplet concentrations were used for continental and marine thunderstorms respectively. The new formulation was then tested by comparing the annual global flash number and diurnal cycles to corresponding results issued from year worth of observations of the Optical Transient Detector Satellite (OTD, see section 6.1.3). It was concluded that the new formulations including cloud droplet concentrations agreed well with observations and was significantly better than the formulation by Price and Rind [1992]. The improvement was largely attributed to a more accurate parameterization of marine thunderstorms. A recent OTD climatology suggests that especially equatorial marine thunderstorms can
Ozone and nitrogen oxides in the tropopause region exhibit appreciable flash rates [Christian and Lantham, 1998] making it thus necessary to correctly represent them in GCMs.

Tapia et al. [1998] reported striking similarities between spatial distribution of rainfall estimates for rainfall maps derived from the WSR-88D radar at Melbourne (FL) and lightning observations made by the US National Lightning Detection Network (NLDN, see section 6.1.3). Based on the observation of 22 thunderstorms observed during August 1992 and 1993, the correlation was demonstrated to withstand both diurnal and interannual variability of both parameters. Although the correlation was originally used for estimating convective rainfall based upon lightning observations, the procedure could also be inversed and used as a lightning parameterization based upon observed (radar) or parameterized convective rainfall.

Another, (similar), approach for parametrizing flash rates was recently implemented by Allen et al. [in press]. They used observed CG flash rates from the NLDN and upward cloud mass fluxes from the Relaxed Arakawa-Schubert convective parameterization in the NASA GEOS-STRAT assimilation. A fourth order polynomial fit was used to correlate observed and simulated data sources for a four day period in November 1997. Ranked values rather than paired values were used because the convective parameterization in the GEOS-STRAT assimilation does not necessarily put the convective cells in the same grid cells as corresponding, observed flash rates. Such spatial shifts are also common in numerical weather prediction models (see discussion in 7.2).

Separate marine and continental relationships between observed flash rates and cloud mass flux were developed, but they were similar. This is an encouraging result but it is noted that it needs a validation for longer periods of time and for other geographic regions. Moreover, uncertainties in the detection efficiency of the NLDN for lightning occurring offshore (marine locations) of the land based detection system need to be considered during such a validation.

Despite recent progress towards reliable parameterizations of lightning flash rates, there remain important uncertainties. Throughout the thesis, observed rather than parameterized lightning flash rates will therefore be used. Respective detections are briefly discussed in section 6.1.3.
3 NOXAR measurement system

This chapter summarizes design constraints and operation principles of the NOXAR (Nitrogen Oxides and Ozone along Air Routes) system which was developed during the thesis research of Dominik Brunner [Brunner, 1998] in cooperation with ECO PHYSICS, Dürnten, Switzerland [Dias-Lalcaca et al., 1998]. The sub-section on the NO analyzer follows the principles outlined by used in Drummond et al. [1985] and Brunner [1998].

3.1 Overview

Building a completely automated instrument for a commercial airliner is a challenging task since both stringent fire and mechanical safety standards must be met and high reliability of the instrumentation is required. Ground-times between intercontinental flights are of the order of a few hours, during which only minor maintenance work can be performed. Due to the permanent installation of the NOXAR system in a Swissair B-747 357 (combi) airliner, the system had to be fully automatic, with the lowest possible weight and power consumption while not exceeding a given volume. To achieve these aims, the instrumentation package was designed to use commercial NO, NO$_2$ and O$_3$ analyzers, modified where necessary and installed together with all the auxiliary equipment (vacuum pumps, power supplies, pure air generator, calibration unit, control computer) in a purpose-built rack designed to meet the stringent civil aviation safety standards [Dias-Lalcaca et al., 1998]. NO was measured by an instrument ECO PHYSICS CLD 780 TR analyzer. NO$_2$ by the same type of instrument after photolytic conversion (instrument ECO PHYSICS PLC 762) and ozone by a modified Environics S-300 UV absorption device (see 3.5).

The rack was installed at the back of the cargo-bay (Figure 3.1) where both the large power dissipation of the instrument and the noise from pumps, compressors and cooling ventilators did not interfere with passengers' comfort.

![Cargo Bay NOXAR Rack](image)

Figure 3.1. Schematic representing the location of passenger seats and cargo bay of the Swissair B-747-357 (combi) aircraft. The cargo bay (dotted line) gives room for seven standard air-cargo containers (boxes, thin lines). The NOXAR rack located at the very back is symbolized with a filled black rectangle.
3.2 Gas-flow

Figure 3.2 represents the gas flow diagram of the system, showing the sample flow, inlet pressure stabilization system, zero air supply, and gas path. The air sample is obtained through an aerofoil-sectioned aluminum boom with a PTFE core, mounted on an aluminum plate, which replaced the second window just forward of the aircraft's rearmost starboard door. The boom extends 9 inches (approximately 23.5 cm) into the slipstream from the aircraft skin to avoid contamination with air in contact with the aircraft body. Air is drawn into the rearward facing 5/8" i.d. (inner diameter) aperture at the tip of the boom and is then carried through the boom and to the instrumentation rack through a 5m long sample line (3/4" o.d. (outer diameter) PTFE tubing with an inner diameter of 5/8").

The sample pressure at the inlet to the NO and NO\textsubscript{2} analyzers is held constant at 85 hPa by the use of a critical orifice and a bypass system in which air in excess of that required by the instrumentation is pumped away, through a motor-driven needle valve. The relatively large sample flow rate of 12 l/minute (STP) at 200 hPa ambient pressure keeps the residence time in the sample line constant at 0.9 seconds irrespective of ambient pressure [Dias-Lalcaca et al., 1999]. The branch of sample air delivered to the ozone analyzer is compressed to cabin pressure (800-850hPa) by a Teflon-coated diaphragm pump (C2) before entering the detector in order to improve instrument sensitivity.

A PTFE solenoid valve (Fig. 3.2 V1) located near the sample line inlet is opened after take-off and closed before landing to avoid contamination of the sample line in the planetary boundary layer and the heavily polluted airport environment. Similar to Ridley et al. [1994] the sample line is reverse-flushed with zero air during warm-up phase when the aircraft potentially crosses humid and polluted air of the lower troposphere. A second, PTFE solenoid valve (V2) is used to switch between sample and calibration gas.

The calibration system consists of a Pure Air Generator (type PAG 002, ECO PHYSICS AG, Switzerland), a compressor, a multi-gas calibrator S-100 (Environics Inc., USA) and a calibration gas cylinder (1 L of 6 ppmv NO in N\textsubscript{2} at 50 bar, Carbagas, Switzerland). In the Pure Air Generator (PAG) ambient air from the cargo compartment is aspired and purified by several processes: Nitric oxides and other oxidizable gases are oxidized by ozone produced by a high performance UV lamp welded into a PVDF vessel. The gas is also passed through an activated charcoal in a sealed PVC container. Humidity contained in the gas is removed to a dew point of -15°C by two processes: By expanding (and thus cooling) the compressed air from 6 bar to 2 bar and by additionally cooling it with Peltier elements. Purified air is primarily used for calibrations (reference cycle of the ozone instrument and the zeroing-, span-, and gas-phase titration
Figure 3.2. Flow diagram of NOXAR system adapted from Brunner [1998]. P=Pump, C=Compressor Pump, B=Flow restriction (critical orifice), V=Valve, CLD=Eco Physics chemiluminescence detector, S-300=Environics ozone analyzer, S-100=Environics calibration gas mixing device (calibrator)
calibrations of the NO analyzers) performed periodically during the flights. Besides the PAG continuously feeds the TRs’ ozonizers and photomultiplier cooling systems. The S-100 calibration unit is used to dilute NO calibration gas with PAG zero air for span calibrations and also contains an ozone source used for the titration of NO during calibrations of the conversion efficiency of the photolytic converter [Brunner, 1998].

3.3 Control and data acquisition system

System control is maintained by a computer which is also interfaced to the digital flight data recorder (DFDR) bus (via a test output on the crash recorder unit) and the Airshow-System, which provides positional data for the visual presentation of a few selected flight parameters to passengers during the flight. The NOXAR system is automatically switched on and off based upon the position of the weight activated in-air switch from the landing gear, and the flap-position. All measurement data and system parameters are stored on a removable PCMCIA hard disk, which is exchanged at daily to weekly intervals to pick-up the measurement data.

3.4 System security

The computer also monitors system pressure and temperature and shuts the system down when the temperature of any sensor exceeds 50° C or the cabin pressure drops below 600 hPa indicating trouble with the aircraft. Moreover, low pressures can cause disruptive discharges, which would damage the high voltage devices. For added security, pressure and temperature are also monitored by an independent electrical circuit, which can trigger an immediate emergency shutdown of the system (stopping the rack ventilation system and causing the rack to close). This would also trigger an audible and visible alarm in the galley next to the cargo compartment and could only be stopped when acknowledged by the cabin crew. Once shutdown in such a manner, the system can only be reactivated manually from within the rack. The main galley power switch of the system, which supplies the NOXAR system, is located in the cockpit from where the supply can be interrupted at any time. The third level of fire defense is provided by six (compact) independent temperature-activated extinguishers, which would fill the rack with Halon vapor at temperatures in excess of 73° C.

Prior to the first campaign the system had to be tested for conducted and radiated interference at Oerlikon-Contraves AG, EMC Test Center in Zürich and again when installed in the aircraft. Since only minor electrical modifications had been performed since the first campaign, only the latter test had to be repeated for getting operation permission for POLINAT 2. Last but not least every visit to the aircraft was reported in a checklist which was sent to the Swiss Federal Office of Civil Aviation (FOCA).
3.5 Ozone analyzer

A modified Environics S-300 UV-absorption device was used for the ozone measurement. The resonance line of a low-pressure mercury lamp (253.7nm) provides UV light close to the maximum of the Hartley absorption bands of ozone. In the device the amount of UV light absorbed by ozone molecules flowing through a sample tube is recorded and contrasted to the transmittance of ozone-free reference air. Instead of using the standard technique of switching the sample flow through an ozone scrubber to create “reference” air for the instrument’s zero signal, air from the pure air generator (PAG) was used to preclude the possibility of the scrubber slowly becoming saturated due to frequent encounters of elevated stratospheric ozone concentrations [Dias-Lalcaca et al., 1998]. The ozone concentration can be calculated from sample and reference signals by combining the Beer-Lambert equation with the ideal gas-law:

\[
O_3 [\text{ppbv}] = \frac{1}{\alpha \cdot l} \cdot \ln\left(\frac{I}{I_s}\right) \cdot \frac{T}{T_0} \cdot \frac{p}{p_0} \cdot 10^9 \text{ppbv} \tag{3-1}
\]

where

- \(O_3\): The ozone concentration in ppbv.
- \(\alpha\): Absorption coefficient of O3 at 253.7 nm (=308 cm\(^{-1}\) at 273 K and 1013 mbar)
- \(l\): Length of the absorption path [cm]
- \(I_s, I\): Intensity of sample and reference signals respectively
- \(p, T\): Pressure [mbar] and temperature [K] in the absorption cell
- \(p_0, T_0\): Standard pressure and temperature (1013 mbar, 273K)
- \(10^9\): This factor converts measured values into the VMR (volume mixing ratio) unit ppbv

Note that the ratio between \(I_s\) and \(I\) is used in expression (3-1), so that the absolute value of the (varying) light intensity does not need to be calibrated. However, the term \((\alpha \cdot l)^{-1}\) (which includes the tube length and absorption coefficient) as well as the pressure and temperature sensors of the ozone device were calibrated against the primary NIST-14 (US National Institute of Standards and Technology) ozone reference instrument at the Swiss Federal Office for Standards (EAM, Bern) at the end of the POLINAT 2 campaign.
3.6 NO analyzer

A commercial ECO PHYSICS CLD 780 TR analyzer (referred to as TR throughout the text) was used to measure nitric oxide concentrations. This instrument detects the chemiluminescent signal generated when NO-containing sample gas is mixed with an excess of internally generated ozone in a reaction chamber held at constant temperature and known pressure and is thus similar to the concept used by Drummond et al. [1985].

3.6.1 Theoretical background

The detection of NO is based on the chemiluminescence observed during its oxidation by O₃. It is induced by adding an excess of O₃ to the sampled airflow. The reactions involved are given by:

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(R2.25a)} \\
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2^* + \text{O}_2 \quad \text{(R2.25b)}
\end{align*}
\]

\[
\begin{align*}
\text{NO}_2^* & \rightarrow \text{hv} + \text{NO}_2 \quad \text{(R3.1)} \\
\text{NO}_2^* + \text{M} & \rightarrow \text{NO}_2 + \text{M} \quad \text{(R3.2)}
\end{align*}
\]

Brunner [1998] has noted that the following updated set of rate constants should be used, which replace the values indicated by Clough and Thrush, [1967].

\[
\begin{align*}
k_{3.1}+k_{3.2} &= 1.8 \times 10^{12} \exp(-1370/T) \quad \text{[Atkinson et al., 1996]} \\
k_{3.2} &= 2.9 \times 10^{12} \exp(-1951/T) \quad \text{[Clough and Thrush, 1967]} \\
1/k_{3.3} &= 6.5 \times 10^{-2} \text{ sec (lifetime of excited state)} \quad \text{[Kaufman, 1976]} \\
k_{3.3}/k_{3.4} &\approx 1.3 \times 10^{14} \text{molecules cm}^{-3} \quad \text{[Schurath et al., 1981]}
\end{align*}
\]

Thereafter about 6% (rather than 25%, obtained with the originally indicated rate-constants) of NO₂ are produced in an excited state (NO₂*) at room temperature (R3.2) and the remaining, large majority of NO, is oxidized to ground state NO₂ (R3.1). At pressures above 1 mbar about 1% of the excited NO₂* molecules decay to ground state NO₂ with photoemission taking place in a broad band between 600 and 2800 nm (R3.1). All other excited molecules lose their energy through collision (quenching) with N₂, O₂ and H₂O which are present in the reaction chamber. Using these chemical reactions, the signal obtained from NO was described by Ridley and Howlett [1974] and Drummond et al. [1977]:

\[
S_{\text{NO}} = \alpha_{\text{NO}} V \mu_{\text{NO}} \frac{\text{NO}_2^*}{(k_{3.1} + k_{3.2})k_{3.4}} \left(1 - e^{-(k_{3.1} + k_{3.2})[O_3]_t}ight) \quad (3-2)
\]
The proportionality factor $a_{NO}$ contains the spectral sensitivity and the geometry of the instrument, $V$ is the volume flow rate, $\mu_{NO}$ is the mixing ratio of NO, and $k_{3,1}$ through $k_{3,4}$ the rate coefficients given above. The exponential term describes the fraction of ambient NO leaving the detector before having reacted with ozone. There, $t_R$ is the residence time of the sampled air and $[O_3]_R$ is the ozone concentration in the detector.

In the TRs volume flow rate, excess ozone as well as pressure and temperature (and thus the rate constants $k_{3,1}$ through $k_{3,4}$) are kept constant so that expression (3-2) can be simplified to:

$$S_{NO} = F_{NO} \mu_{NO} \tag{3-3}$$

The proportionality factor $F_{NO}$ [cts ppbv$^{-1}$] between NO-signal ($S_{NO}$) and the NO mixing ratio ($\mu_{NO}$) contains all constants and shall be termed *sensitivity of the instrument*. For the TRs used in the NOXAR system, $F_{NO}$ is about 1 cts·s$^{-1}$·pptv$^{-1}$ when operated at a flow rate of 3 l/min STP (at 15mbar and $T=323\text{K}$). This is only about $10^{-4}$ of the theoretically calculated value by Ridley and Howlett [1974]. Reasons for this large discrepancy are summarized in Brunner [1998].

In addition to the signal of NO ($S_{NO}$), the instrument records other (unwanted) signals. These are the dark current of the photomultiplier ($S_D$) and chemiluminescence from interfering reactions ($S_I$) [Drummond et al., 1985]. The total signal $S_m$ obtained in measure mode is therefore:

$$S_m = S_{NO} + S_D + S_I \tag{3-4}$$

Since not separable with turned-on ozonizers (as is always the case during flight), the photomultiplier dark current $S_D$ and the signal from interfering substances $S_I$ shall collectively be labeled as background signal ($S_B$). Indices M and P employed later in the text will indicate whether the background signal was detected in measure or pre-reactor mode (the other way round if no indices are present, the statements will refer to both modes):

$$S_B = S_D + S_I \tag{3-5}$$

The photomultiplier dark current ($S_D$) and interfering substances lower the signal to noise ratio $S_{NO} / \sqrt{S_m}$ and should therefore be minimized. $S_D$ is largely dominated by

\[1\) Following poissonian statistics the standard deviation of a variable is equal to the square root of it.
spontaneous emissions of thermionic electrons from the photocathode and dynodes of a photomultiplier tube. Cooling the photomultiplier tube can reduce these thermionic emissions and thus \( S_D \). In the TRs a level of 200 cts-s\(^{-1}\) (during ground operation in the laboratory) is achieved at a temperature of \(-40^\circ\) C \([\text{Dias-Lalcaca et al., 1998}]\). Ridley et al. \([\text{1994}]\) have noted that the photomultiplier dark count rate is influenced by cosmic ray events. The cosmic ray influence was found to be small between the surface and 4 km but caused nonlinear increases in count rates by a factor of 2 and increases in the standard deviation by a factor 2-3 at 12 km (see also section 4.3.3).

Drummond et al. \([\text{1985}]\) distinguished between three categories of \( S_I \): internal interferences, interference by chemiluminescent reactions of atmospheric species (other than NO), and wall catalyzed formation of NO from nitrogen-containing species. In contrast to \( S_D \), \( S_I \) constitutes a much more significant part to \( S_B \). Unlike the signal from the photomultiplier dark current, \( S_I \) cannot be measured directly \([\text{Drummond et al., 1977}]\) and thus needs to be calibrated in a zero mode. During NOXAR in 1995-96, \( S_B \) was determined during the so-called zeroing calibration with air produced from the Pure Air Generator (PAG). For POLINAT 2 a calibration type similar to that suggested by Drummond \([\text{1977}]\), making use of the instrument’s internal pre-reactor, was implemented (see section 4.3.2) and shall be labeled zero calibration.

### 3.6.2 Measurement and calibration modes of the TRs

The gas-flow diagram of the TRs is given in Figure 3.3 and can be used to illustrate measurement- and pre-reactor modes, which are used for measuring and calibrating respectively. In the measurement mode, valves \( V_1 \) and \( V_2 \) are switched such that sample air (In) and ozone from the ozonizers (O\(_3\)) mix in the main reactor, where the chemiluminescence is detected by the photomultiplier. In the pre-reactor mode both gases first mixed in the pre-reactor (pre-r. in Figure 3.3) where the residence time is nearly sufficient to complete the chemiluminescent reactions (R2-25a,b) and (R3.1). Thus, only a small fraction (1-\( \lambda \)) (\( \approx 5\% \) in the TRs) of the chemiluminescence takes place in the main reactor, where it is being detected by the PMT (the design thus slightly differs from the concept proposed by Drummond et al. \([\text{1985}]\), where \( \lambda \) is very close to unity). During NOXAR in 1995-96 the instruments were operated continuously in measure-mode interrupted every 20 minutes by a zeroing calibration \([\text{Brunner, 1998}]\) which will be described below.
3.6.3 Zeroing calibration

During instrument zeroings, the inlet and calibration valves (V1 and V2 in Figure 3.2) are switched such that NOX-free air from the pure air generator (PAG) instead of ambient air is passed through the sampling lines to the NO and NO2 analyzers. The signal \( S_m \) is recorded both in measure and pre-reactor mode during 15 seconds each. For operation in measure mode, Equations (3-4) and (3-5) simplify to:

\[
S_m = S_{BM} \quad (3-6)
\]

so that the measured signal (\( S_m \)) is equal to the background signal of the main-reactor mode. Similarly, the background signal of the pre-reactor mode (\( S_{BP} \)) can be obtained by mixing ozone and PAG-output in the pre-reactor.

\[
S_m = S_{BP} \quad (3-7)
\]

The background signals of the instruments operated in pre-reactor- (\( S_{BP} \)) and measure mode (\( S_{BM} \)) exhibit a difference [Drummond et al., 1985] of up to 100 pptv [Brunner, 1998], the reason of which is largely unknown. This difference shall be labeled \( S_{diff} \) and needs to be calibrated regularly.

\[
S_{diff} = S_{BP} - S_{BM} \quad (3-8)
\]
A large fraction of $S_B$ is most probably caused by chemiluminescence reactions of ozone on the reactor walls [Drummond et al., 1985]. Obviously the frequency and/or location of these internal chemiluminescence reactions changes for the different gas-paths in measure- and pre-reactor mode, which may partly explain the difference. A disadvantage of the zeroing calibration lies in the fact that the purified air from the PAG is not representative for interfering substances potentially contained in ambient air. However, Brunner [1998] concluded from a compilation of published values on interfering substances, that all investigated species produce negligible interference with the NO measurement for the concentration range expected in the upper troposphere and the lower stratosphere. There always remains a certain measure of doubt whether an important interfering species has been overlooked or whether synergistic effects between different species could play a role. The crucial and final test has therefore to be on flight legs, where no NO is present, i.e., a night time flight above the boundary layer [Drummond et al., 1985]. With night time measurements being close to zero, the system seemed to be fairly immune to interfering substances [Brunner, 1998], at least for nighttime chemistry at cruising altitude.

### 3.6.4 Sensitivity (span) calibration

The sensitivity of both TRs is calibrated in-flight at three hour intervals by administering calibration gas with a known NO volume mixing ratio $\mu_{\text{NO}}$. Due to flight safety restrictions only one liter of pressurized (max. 50 bar) calibration gas could be carried within the rack. Calibration gas usage was minimized by employing N$_2$ gas containing 6 ppmv NO, which is about a thousand times the concentration needed during the sensitivity calibration. Besides, higher gas concentrations remain more stable over the course of time. Bottles were typically exchanged at three to four weeks intervals. Before and after integration these bottles were calibrated against a 100 ppmv reference NO bottle (in N$_2$). The latter was shipped to DLR for intercomparison at the end of the POLINAT2 campaign and all measurements scaled accordingly.

During the sensitivity calibration, gas from the 1-liter cylinder is diluted to 20 ppbv with air from the PAG. Calibration gas is introduced into the sampling line as close to the inlet as possible to account for possible (heterogeneous) wall effects [Dias-Lalcaca et al., 1998]. The instrument is operated in measure and pre-reactor mode and both signals are integrated over 15 seconds. From the calibration, the fraction $\lambda$ of NO reacting in pre-reactor mode can be obtained as follows [Brunner, 1998]:

$$\lambda = \frac{S_M - S_P - (S_{RM} - S_{RP})}{S_M - S_{RM}}$$  \hspace{1cm} (3.9)
where the signals $S_M$ and $S_P$ are measured during the sensitivity calibration and $S_{BP}$ as well as $S_{BM}$ are linearly interpolated between two subsequent zeroing calibrations to the time of the sensitivity calibration. The sensitivity of the device ($F_{NO}$) can then be obtained from $\lambda$, the measured signals and the known NO volume mixing ratio $\mu_o$.

$$F_{NO} = \frac{S_M - (S_P - S_{\text{diff}})}{\mu_o \lambda}$$  \hspace{1cm} (3-10)

The sensitivity calibration is performed at 3 hour intervals and for the first time after three hours. Both $\lambda$ and $F_{NO}$ remain relatively constant between the calibrations.

### 3.6.5 Calculating the NO mixing ratio

The NO volume mixing ratio in ambient air ($\mu_{NO}$) can be obtained with (3-11) by linearly interpolating the calibrated values $F_{NO}$, $S_{BP}$ and $S_{\text{diff}}$ to the time of the measured NO signal ($S_M$):

$$\mu_{NO} = \frac{(S_M - S_{BM})}{F_{NO}} = \frac{(S_M - S_{BP} + S_{\text{diff}})}{F_{NO}}$$  \hspace{1cm} (3-11)

### 3.7 Photolytic NO$_2$/NO$_3$ converter

At cruising altitude during nighttime, NO is oxidized to NO$_2$ and NO$_3$ due to the titration of NO with ambient ozone. By measuring NO$_2$ at night, the number of NO$_x$ measurements obtained with the NOXAR can therefore about be doubled. Kley and McFarland [1980] proposed to photolytically (with UV light of 300-400 nm) convert NO$_2$ to NO which can subsequently be measured with an NO analyzer. Field campaigns and laboratory experiments have shown that such converters are highly specific for the conversion of NO$_2$ to NO [Ridley et al., 1988a; Feisenfeld et al., 1990]. (Note that the conversion efficiency of NO$_3$ is nearly 100%. To facilitate reading only NO$_2$ will be mentioned, but NO$_3$ is equally meant.) For the NOXAR system ECO PHYSICS used a photolytic converter type PLC.

The basic reactions involved in the photolysis of NO$_2$ to NO in the converter are:

\begin{align*}
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} & \text{(R3.3)} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} & \text{(R3.4)} \\
\text{NO}_2 + \text{hv (}+\text{O}_2) & \rightarrow \text{NO} + \text{O}_3 \text{ (net)}
\end{align*}
NO can also be oxidized to NO₂ and thus decreases the conversion efficiency of the detector.

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  
(R3.5)

The NO detector operating with a photolytic converter measures the sum \([\text{NO}_c]\) of ambient NO and that produced from the conversion of NO₂:

\[ [\text{NO}_c] = \text{NO} + \Delta \text{NO} \]  
(3-12)

The conversion does not take place at 100% and a conversion efficiency is therefore introduced:

\[ CE = \frac{\Delta \text{NO}}{[\text{NO}_2]_0} \]  
(3-13)

where \([\text{NO}_2]_0\) denotes the NO₂ present at the entry of the converter and \(\Delta \text{NO}\) the amount of NO produced from NO₂.

The conversion efficiency can be written as a function of the residence time \(\tau\) in the photolytic converter and the photolysis rate \(J_{\text{NO}_2}\)

\[ CE = 1 - \exp(-J_{\text{NO}_2} \cdot \tau) \]  
(3-14)

where the residence time \(\tau\) is the ratio between the volume of the PLC and the volume flow rate, which is stabilized with the by-pass regulating system (This is an approximation. An analytically correct formula can be found in [Brunner, 1998]). Twice a flight the photolysis rate \(J_{\text{NO}_2}\) was calibrated using a gas phase titration as described in the United States Environmental Protection Agency publication EPA-E600/4-75-003. The conversion efficiency is then calculated for every measurement by interpolating between these two calibrations and considering actual, measured values of the volume flow rate.

The NO₂ mixing ratio in the sample gas can be calculated from the measured signal \(\text{NO}_c\) (TR2), NO (TR1) and CE using equations (3-12 ) and (3-13). The PLC volume causes an attenuation of the measurement signal on TR2. For the calculation of \(\Delta \text{NO}\) the signal of TR1 was smeared out. Details on this process can be found in Brunner [1998].
4 Modifications for POLINAT 2 & Data Quality

In this chapter modifications to the NOXAR campaign in 1995-96 are presented. The chapter includes also the motivation for the adaptations, laboratory tests as well as instrumental performance in air and intercomparisons with other field measurements.

4.1 Modifications: Overview

Several modifications of the existing system were performed prior to and during the POLINAT 2 campaign:

- To account for a possible altitude bias of the ozone measurements (see section 4.2.1) the glass sample tube of the ozone analyzer was replaced by the original Environics® Teflon coated tube (and the sample flow reduced from 3 to 1 l/min).
- In order to accurately follow the TRs’ drifting background-signals 30 instead of 3 calibrations per hour were performed. This could be achieved with a new calibration type making use of the devices’ internal pre-reactors.
- To measure vertical NOx-profiles down to 3000 m the installed by-pass pump (16 m³/h, STP) was replaced by a more powerful device (25 m³/h, STP).
- In an attempt to decrease the signal difference between pre- and main-reactor mode during the zeroing calibration, the internal tubing of the NOx analyzers was changed by ECO PHYSICS so that the pre-reactor was permanently flushed.
- All sample lines were replaced with new PTFE tubing and valves were cleaned to minimize heterogeneous reactions on the walls.

4.2 Ozone measurement

Prior to the campaign the vertical profiles obtained during descent into Zurich airport were compared to the vertical ozone profiles of ozone soundings launched at the Aérological Station in Payerne, Switzerland (section 4.2.1). An altitude bias of the NOXAR measurements was observed and in view of these finding laboratory experiments performed to identify its cause (section 4.2.2).

4.2.1 Comparison with Payerne ozone sondes

The vertical ozone profiles from Brewer-Mast sondes [Brewer and Milford, 1960] launched operationally at the Aérological Station in Payerne, Switzerland, [Stuebi et al., 1996] were compared to the ones obtained from NOXAR (1995-96) during descent into Zurich airport.
Raw ozone profile data are processed in a number of steps at the Aérological Station. These involve:

- A pump correction, *which* accounts for losses in the pump efficiency at ambient pressures lower than 100 hPa.
- Dobson normalization: Individual ozone soundings are scaled to match the concurrent measurements of the ozone column made at the Light Observatory in Arosa, Switzerland. The reason for this correction is that one assumes that the relative measurement is correct, but the absolute amount measured depends on the individual efficiency of the sonde. The overall precision of the Dobson normalization was evaluated to about 5% [Beckmann et al., 1994].
- Laboratory calibration: Prior to their launch the sondes are calibrated against a reference ozone-meter in the laboratory and results from the sounding corrected accordingly.

It is still under discussion whether this laboratory calibration improves the quality of the soundings. Therefore, the comparisons were performed with both sounding versions (with and without a laboratory calibration). The comparison focused on "similar" and thus air masses with comparable ozone concentrations and was performed as follows:

The best spatial and temporal match between Payerne sondes (launched at 12 UTC) and NOXAR measurements (descent over France starts about 6-8 UTC) could be achieved with flights returning from the United States. Data from 51 such days (where measurements from both platforms were equally available) were processed. Ozone, horizontal wind components and temperature of the ozone sondes were linearly interpolated to the pressure levels of the (3-second averaged) respective NOXAR measurements. The difference of corresponding wind and temperature measurements between both platforms was used to exclude unrelated air masses. In addition, the distance between air parcels from both platforms was calculated as follows: The vertical wind profile determined from the positions of the ascending Payerne balloon was used to obtain the location of these sampled air masses at the time of the (earlier) NOXAR measurement. Great circle distances (shortest distance between two points on a sphere) between the newly obtained positions and the respective NOXAR measurement locations were then calculated. (The same procedure was also performed with NOXAR winds and good agreement with the previous variant was found).

Only a limited number of days exhibited closely corresponding vertical profiles of both wind and temperature. The data set was therefore reduced to the best 15 days on which the maximum temperature difference on same pressure levels did not exceed 2.5°C. For the comparison of corresponding air masses, more restrictive filter criteria were introduced: The aforementioned great circle distance between measurements performed on
the same pressure level had to be smaller than 250 km, and the respective air temperature difference less than 0.75° C. For every vertical profile, the tropopause level was visually identified based upon the measured ozone concentrations. Only tropospheric measurements were used so as to avoid comparing samples from within the steep ozone gradient in the lower stratosphere.

The results of a comparison between NOXAR and Payerne ozone with the Dobson normalization can be found in Figure 4.1. It can be seen that there is a significant altitude dependence of the (relative) difference between the Payerne ozone soundings and the (pseudo) vertical NOXAR profiles. Sensitivity studies showed that this result is stable with respect to the selection of the aforementioned criteria and threshold values used for filtering the two data sets.

Since only similar air masses from a rather small area were compared, the observed altitude trend is most likely attributable to systematic measurement errors rather than real ozone-gradients. However, ozone sondes have their best performance in the stratosphere and estimates of the precision in the troposphere are in the range of 4-12% [Barnes et al., 1985; Beekmann et al., 1994; Komhyr et al., 1995] with higher values shown for Brewer-Mast sondes in the 1991 intercomparison, 8-18% [WMO, 1995]. Even though uncertainties associated with sondes are therefore quite large, the altitude trend of the difference calls for an evaluation of its cause. In the following chapter a bias of the NOXAR system as a possible cause for the observed difference is investigated in laboratory experiments.
Figure 4.1. Box plot of the relative difference between the Payerne ozone-sounding and respective NOXAR vertical profiles from the campaign in 1995-96. Vertical white lines indicate median values, the gray boxes represent the distance between the first and the third quartile, dotted lines extending from the top and bottom of the box) are called whisker and extend to the extreme values of the data or 1.5x the interquartile distance from the center, whichever is less. Data points, which fall outside the whiskers, may be outliers, and are indicated by vertical lines. The thickness of the boxes is representative for the number of data points in each altitude class.

4.2.2 Laboratory studies and modifications

Causes for this (possible) altitude bias were investigated in laboratory experiments prior to the POLINAT 2 campaign: A leak identified at the fitting of the modified absorption tube could hardly explain the difference. By simulating varying flight altitudes (and thus causing different compression ratios of ambient air), no evidence of an altitude dependence of the ozone destruction in the compressor (C2 in Figure 3.2) and the sample lines could be found for the investigated pressure range between 250 and 600 hPa. These findings are in agreement with experience gained from the MOZAIC team (Philipp Nedelec, Univ. Toulouse, personal communication, 1998). The experiment was repeated with the compressor still in the warm-up phase and after having reached steady-state temperature. Interestingly, this parameter did not seem to affect the ozone destruction in any significant manner.
However, the altitude bias of the ozone measurement is more likely a consequence of the glass absorption tube used during the first campaign. By varying the humidity content of several ozone-free samples, the device measured significant ozone concentrations, even exceeding the observed difference to the Payerne soundings. Higher humidity in the sample than in reference air (which is more or less stabilized at -15°C with the PAG) always caused a positive, significant ozone offset. The magnitude of this effect increased with the humidity content in the sample gas and is thus consistent with the higher NOXAR-O₃ measurements during descents when the humidity concentration increases.

Inspection of the sampling block showed that without the tube in place, only a minor fraction of the unfocussed UV light reached the photometer at the other end of the tube. Light is therefore transmitted through reflection at the tube’s walls. The humidity concentration of both sample and reference air likely change the reflective properties of the tube’s walls and thus influence the ozone measurement. Different types of glass as well as their history to previous ozone exposures, changed the magnitude of the ozone offset. Similar observations of humidity effects have been reported by Meyer et al. [1991] where the varying extinction of UV light by the windows of the optical cell was identified as the reason for erroneous measurements.

Optimization experiments in the laboratory led to replacing the existing glass tube with the original Environics PTFE coated ozone absorption tube, with which this humidity effect could be minimized (see section 4.4.1 for an assessment of the performance of modified instrument during POLINAT 2).

### 4.3 NOₓ measurement

Here laboratory measurements of the TR analyzer are described as well as an implementation of a calibration type making use of the instrument’s pre-reactors as has been proposed by Drummond et al. [1977].

#### 4.3.1 Zeroline: Laboratory measurements

Laboratory measurements were performed to better characterize the TRs’ background signals \( S_b \), which are needed to calculate the volume mixing ratio of ambient NO and NO₂. The measurements provided evidence that the background signals of the TRs both in measure- \( S_{bM} \) and pre-reactor mode \( S_{bP} \) depend on the water vapor concentration contained in the sample gas. This finding is in line with the following publications: (a) Drummond et al. [1985] suggested that by humidification of the effluent of their ozonizer, potential contaminants and thus interfering substances could be removed and the background signal lowered. (b) Ridley et al. [1994] reported that electronically excited NO₂⁺ is quenched more efficiently by water than “dry air” (R3.2). Although the
effect was small, in their instrument, the authors purposely added water at a constant flow (2-3 % of total flow) to improve instrument stability, to shorten start-up settling time, to decrease background count rates, and to make the instrument relatively insensitive to cloud penetrations.

In the experimental setup (Figure 4.2) the background signal caused by different types of NOx-free gases was measured: Ambient air filtered with a Purafil® cartridge, air from an ECO PHYSICS pure air generator (PAG) and pure N2 from a bottle, with dew-points of -3° C, -21° C and -56° C respectively. These gases were connected to the sample-ins of both TRs and the typical operating pressure of 85 mbar (at the inlet of the device) simulated with a tap positioned between the analyzers and the gas source.

![Diagram](image)

**Figure 4.2.** Experimental set-up: NOx-free gas sources are located on the left-hand side (the shaded box symbolizes a Purafil cartridge, below is the PAG and at the third tap a N2 bottle). Two taps are entirely closed and one slightly opened to produce a pressure of 85 mbar at the instruments’ inlets.

During the experiment the inlet pressure (P) was closely monitored because it also affects the instruments’ background signals. (Prior to the measurements, tubes and connections, which conducted NOx-free gas at 85 mbar, were leak-tested by venting elevated NO concentrations around the tubing). The first measurement with filtered ambient air was carried out several hours after both analyzers had reached a stable signal level. Switching to the drier NOx-free gases caused rapid jumps of the background signals, which were recorded five to ten minutes after having reached steady-state.
Table 4.1. Humidity dependence of the background signals $S_{BP}$ and $S_{BM}$ of TR1 and 2. $S_{diff}$ is the difference between $S_{BP}$ and $S_{BM}$. Signals averaged over 6 measurement cycles with 20 seconds integration time are tabulated. “before” and “after” denote parameters measured at the beginning and end of an experiment.

Table 4.2. Effectiveness of the humidification of the sample gas from TR2. TR1 served as a control instrument and its sample flow was not humidified.
Humidifying the flow of the ozonizers requires precautionary measures, which ensure that water does not end up between the high voltage plates (as can happen during reverse flow in case of pump failure or through diffusion when the instrument is on ground). At this location water would damage the ozonizers and probably also other parts of the analyzer.

The experiment was therefore set up more conservatively: NO$_x$-free air was produced in a Purafil cartridge connected to a humidifying box provided by ECO PHYSICS AG which was merged with the sample flow at the sample inlet of TR2 (right-hand side of Figure 4.2). The sample gas of TR1 was not humidified and thus served as a control instrument.

Table 4.2, shows that the background signals of TR2 operated in pre-reactor mode ($S_{BP}$) could be reduced by 22% and by 29% in measure mode ($S_{BM}$) when the dry N$_2$ gas was humidified. During the same period of time the control instrument exhibited a constant noise level. This (non-invasive) humidification of sample air is clearly less effective in reducing the background signals $S_B$ than the values reported by Drummond et al. [1985]. However, in the advent of the coordinated flights with the DLR Falcon and NASA DC-8 this more conservative approach was adopted to minimize the risk of instrumental damage. Both TR1 and TR2 were equipped with a humidifying unit and a critical flow restrictor, which restricts the water vapor supply to 110 ml/s (at a cargo pressure of 850 hPa).

The laboratory experiments also suggest that the (unwanted) difference $S_{diff}$ is roughly proportional to the background signal and thus the water vapor concentration contained in the sample gas. Humidification therefore also helped to constrain this effect.

The findings of the laboratory measurements are consistent with observed rapid decreases of the background signal during final approach of an airport, when the humidity in the sample gas increases over several orders of magnitude (see section 4.4.1). The opposite, an increase of the background signal of 50 to 150 counts/s could occasionally be observed after the aircraft had climbed to a higher cruising level (sometimes entering the drier stratosphere).

The different magnitude of the humidity effect in both situations is in line with much larger changes of the absolute humidity during descent, than the humidity changes occurring at cruising altitude.

### 4.3.2 New zero calibration type

The laboratory results presented in the previous section suggest that the composition ("matrix") of the calibration gas should resemble the sample gas in key constituents (e.g. humidity), for minimizing cross-sensitivities to these species by means of a calibration.
Following the suggestion by Drummond et al. [1977], such calibration gas was produced during the zero calibration by “scrubbing” NO from the sample gas in the TR’s pre-reactors (Figure 3.3), where an excess amount of ozone was added. This way about \( \lambda = 95\% \) (exact value is known from the sensitivity calibration (3-9)) of the contained NO is oxidized to NO\(_2\), before reaching the main reactor where photolytic detection of the remaining 5% takes place. Below, it will be shown how the background signal of the measurement mode \( (S_{BM}) \) can be calculated and the 5% of unreacted NO considered.

A zero calibration cycle interrupted the measurement cycle every two minutes for 30 seconds. This interval contained 20 seconds calibration time and 10 seconds conditioning with zero (before the calibration) and ambient air (after the calibration) respectively.

The measured signal \( (S_{NO(1)}) \) before a zero calibration takes place, is the sum of the background signal \( (S_{BM}) \) and the instrument’s sensitivity \( (F_{NO}) \) multiplied by the (mean) NO mixing ratio \( (\mu_{NO(1)}) \) of the sample gas.

\[
S_{NO(1)} = S_{BM} + F_{NO} \cdot \mu_{NO(1)} 
\]  

(4-1)

The same argument applies for the signal caused by the NO mixing ratio after the zero calibration \( (S_{NO(2)}) \).

\[
S_{NO(2)} = S_{BM} + F_{NO} \cdot \mu_{NO(2)} 
\]  

(4-2)

We assume that the NO mixing ratio in the sample gas during the calibration can be approximated by linearly interpolating the mean NO concentration before \( (\mu_{NO(1)}) \) and after \( (\mu_{NO(2)}) \) the calibration to the time of the calibration and that \( (1-\lambda)*100\% \) of ambient NO is detected in the main reactor. The signal during the zero calibration \( (S_z) \) then becomes:

\[
S_z = S_{BF} + (1-\lambda) \cdot F_{NO} \cdot \frac{1}{2}(\mu_{NO(1)} + \mu_{NO(2)}) 
\]  

(4-3)

The difference between the background signal in pre-reactor and measurement mode \( (S_{diff}) \) is determined during zeroing calibrations and is linearly interpolated to the time of the zero calibration. By combining equations (4-1) to (4-3), the background signal during measurement mode \( (S_{BM}) \) can then be determined:
Note that if the NO concentrations during a zero-calibration are noisy (e.g. when aged aircraft exhausts are crossed), the average concentration is not representative of the background air of the measurements performed before and after the calibration. An example is given here: Assume that the background NO level before, during and after a zero-calibration is 200 pptv. Three out of 20 calibration samples contain NO concentrations of 3000 pptv, which is a typical value when a young aircraft plume is crossed. In this calibration mode about 5% of total NO (contained in the spike) are detected in the main reactor and in consequence, the NO background is overestimated by about 20 pptv. This in turn, leads to a too low zero signal. Crossing of such (young) exhaust plumes, however, occurs relatively rarely and this sort of error should therefore only affect a limited number of zero-calibrations along the flight. On the other hand this type of calibration offers protection against changes in ambient air (such as humidity), the effect of which is not accounted for by a zeroing calibration performed with "artificial zero gas" from the pure air generator (PAG). A draw-back of the zero calibration is that it is not known whether the signal difference $S_{\text{diff}}$ determined with the comparatively humid PAG air is applicable to the zero calibration performed with drier sample gas. This aspect is further discussed in section 4.4.2.1.

4.3.3 Zeroline: Performance in the field

The background signal $S_B$ constitutes a major fraction of the total signal $S_M$ and $S_B$'s evolution must therefore be accurately known for calculating the NO volume-mixing ratio. When the ozone-flow of the TR analyzers is first started, there is an increase in the detector signal. This background signal is independent of whether or not sample gas is flowing, and thus must be caused either by ozone itself or by contaminants in the ozone stream [Drummond et al., 1985], but the effect is still not fully understood. The magnitude of this effect decreases over time: During the flight, TR2 exhibited a decrease of the background signal from an initial level of 6000-9000 cts/s to typically 3500 cts/s (TR1, 2500 cts/s) within the first minutes of operation. Thereafter climb-back progresses much more slowly to levels of 2000 and 1000 cts/s respectively. These values are attained towards the end of a flight but a steady signal level is never reached. Humidification of the sample gas flow, which helped to reduce the background signal in the laboratory, also led to shorter turn-on times during the flights. As an example, two daytime flights from Zurich to Atlanta (October 9 and 14) are presented in Figure 4.3. On the latter flight the humidification flow rate was substantially higher, accounting for about 10% of the sample gas flow rate. Both the initial rapid decrease of the back-
ground signal (A) and the subsequent (slower) decline (B) could be accelerated with respect to the other flight where the humidifying flow only totaled 3% of the sample gas flow.

**Figure 4.3.** Evolution of background signal ($S_{BP}$) of TR2 in pre-reactor mode on two flights. Gray triangles are data from the ZRH-ATL flight of October 09 with a 110ml/s humidification unit provided by ECO PHYSICS AG. Full black circles are data from ZRH-ATL flight on October 14 with 350ml/s flow rate.

Humidification also proved to be helpful for another problem: The steady stream of water vapor constrained the strong decline of $S_{BP}$ (C in figure 4.3) observed during final approach of airports, when the absolute humidity in the sample flow increased over several orders of magnitude. In Figures 4.4 a and b it can be seen that this unwanted change of the background signal could be reduced by about 25% for cases with stronger humidification.

**Figure 4.4.** Decrease of the background signal of TR2 in pre-reactor mode ($S_{BP}$) during descent of the aircraft. $S_{BP}$ is determined every 2 minutes and denoted by black dots. The aircraft altitude is indicated with a line. a) Left panel contains data from October 9 flight and b) right panel data from the October 14 flight.
However, conditioning of the walls with water vapor during cruise and descent was not enough to fully eliminate the effect. This might be partly attributable to changes of the photomultiplier's dark count rate, which should be independent of ozone- and sample-flow. Ridley et al. [1994] operated their instrument without ozone or sample flow at different altitudes and reported that the dark current count of the photomultiplier decreased with lower altitudes, which they attributed to decreasing levels of cosmic-radiation.

Nevertheless, the large number of zero calibrations should make it possible to follow the drifting background signal and thus use the vertical profile information, even though precision is worse than during cruise.

A side effect of the humidification is that the (NO-containing) sample flow rate and thus sensitivity of the device (F\textsubscript{NO}) was reduced from 835 cts/s (October 9) to 760 cts/s (October 14). The main reason of this loss in sensitivity is caused by dilution of the sample by humidified air. The gain in signal to noise ratio, however, offsets this effect. Therefore, a humidifying unit feeding both TRs with 110 ml/s water vapor each (at a cabin pressure of 850 mbar) was installed on September 22. Continuing problems with the still large background signal of TR2 led to increase the flow-rate of the humidifier to (335 ml/s at 957 mbar) on October 11 with which the situation could be improved (cf. Figure 4.3).

4.4 Data Quality Assessment

Data quality is commonly characterized by indicating precision and accuracy. The precision of an instrument reflects the reproducibility of its measurements and is determined by the random spread of repeated identical measurements. The standard deviation of such measurements (e.g. in our case the night-NO measurements) can be used to define precision.

Systematic errors determine the accuracy of a measurement. Systematic errors correspond to the difference between the true value (e.g. determined from a standard instrument) and the mean values obtained from the device of interest.

4.4.1 Ozone Measurement

The ozone analyzer was calibrated against the primary NIST-14 instrument located at the Swiss Federal Office of Meteorology (EAM) in Berne. The accuracy of 1-minute integrated values was determined to be ±4 % for ozone concentrations in the range of 20 to 400 ppbv. Due to corporate policy this test could not be performed with the modified device using the Pure Air Generator instead of the scrubber box for generating the zero signal. This way the humidity effect discussed in section 4.2.2 was not considered in the calibration.
On a number of flights the sample tube was contaminated with aerosols. The changing water vapor concentration between sample and reference signal resulting in oscillations of the ozone signal (typically ±10 ppbv). Affected data was treated in two ways: 10 (3 second averaged) values after a zeroing calibration as well as 4 values after each reference measurement were ignored. The remaining data, which still exhibited an oscillation of ±3 ppbv was smoothed with a (centered) 10 point running average. The latter does not significantly affect the 2 minute averaged data submitted to the archives but removes resolution from the 3 second data, which might be used for more detailed studies (affected data are marked as bad). Moreover reference flow on the November flights was too low due to a badly adjusted pressure regulator. This resulted in ozone values being too low by about 7%. These values were corrected with the in-flight O3 calibration, using ozone generated with the calibrator. This helped to reduce the uncertainty from 7% to 5%.

In order to account for losses in the sample line, a calibration of the entire system with and without the sample line has been performed at the end of the campaign when the aircraft was on ground. As a result, the ozone measurements of the entire campaign were corrected for the estimated loss of 6.5%. (This value is comparable to the 3.5 % correction applied, during the NOXAR campaign in 95-96 [Brunner, 1998]).

4.4.2 NO Measurement

In this section the uncertainty of the NO measurements is discussed both from a theoretical and experimental point of view.

4.4.2.1 Precision of the NO and NO2 measurements

The counting rate $S$ in a photomultiplier tube is subject to random noise, which follows a Poissonian distribution. It can be shown that for such distributions, the standard deviation of the counting rate $S$ is equal to the square root of $S$. The standard deviation ($\delta \mu_{\text{NO},n}$) of a series of $n$ Poisson-distributed measurements (of the same duration) with signals $S_1, S_2, \ldots, S_n$ can be calculated as follows:

$$\delta \mu_{\text{NO},n} = \frac{\sqrt{S}}{\sqrt{n}} \quad (4-5)$$

Expression (4-6) illustrates that the precision of a measurement, which follows a Poissonian distribution, can be improved by averaging over several measurement cycles. This has been used by Ridley et al. [1994] who theoretically derived precision ($\delta \mu_{\text{NO}}$) and detection limit of chemiluminescence detectors. The counting precision (1σ) in pptv of an NO measurement is:
where $\delta_{BM}$ ($\approx \delta_{BP}$) is the error of a single zero calibration and $\delta_M$ the error of a single NO measurement. The error of the background signal ($\delta_{BP}$) derived according to expression (4-6) is 8.6 cts/s for 20 second integration time by assuming a background signal of 1500 cts/s (typical for TRI). Although various definitions of detection limit for chemiluminescence instruments have been reported in the literature, Ridley et al., [1994] suggested using expression (4-7) in the limit that $\delta_{BP}$ approaches $\delta_M$. During our measurements, the NO signal was averaged over 90 seconds so that $\delta_{BP}$=4.1 cts/s. By using $F_{NO}$=0.85 cts/s the theoretical detection limit ($\delta_{NO}$) for POLINAT 2 therefore becomes 9.5 cts/s.

By inserting typical values of TRI from the NOXAR 95-96 campaign into expressions (4-6) and (4-7) Brunner [1998] noted that the theoretically obtained error of 2.9 cts/s (2-min. averaged) was substantially better than the 19 pptv observed during nighttime measurements.

![Normalized histogram of offset-corrected (2-minute averaged) night NO measurements (≤250 pptv) of TRI during POLINAT 2. Offset and non-offset corrected values only differ insignificantly (σ=26 and 29 pptv, mean=-1.26 and 0.35 pptv respectively) sample size=6530 measurements.](image)

Deviations of the real background signal from the assumed linear approximation between two calibrations were listed as a potential candidate for explaining the discrepancy. During POLINAT 2 the interval between two subsequent calibrations was
thus shortened from twenty to two minutes in order to constrain this type of uncertainty. The yield of the modification can experimentally be assessed as follows: At nighttime, NO is expected to disappear due to the rapid titration with ozone (R2.25). Measurements of the NO concentration therefore allow a determination of the analyzer's precision, at least for such nighttime conditions [e.g. Ridley et al., 1974]. For the analysis, all sharp NO spikes (i.e. 2 minute averaged values exceeding 250 pptv) were excluded, since they can typically be attributed to sampling inside young aircraft exhaust which is not yet oxidized to NO₂. A standard deviation of 29 pptv was obtained for all nighttime NO concentrations measured by TR1 (Figure 4.5). The tenfold increase in the number of calibrations did therefore not lead to the hoped for improvement of the instrument's precision. As will be shown below this is most likely a consequence of an instrumental artifact.

Figure 4.6. Upper graphs (a) show night NO measurements performed with TR1 (filled dots) and TR2 (empty dots) as well as a 20 point sliding-averages for the nighttime flight performed on 970912 (left) and 960221 (right). The lower panels show the respective $S_{ref}$ values (determined during the zeroing calibrations). (b) Graphs on the right-hand side show similar analysis for the first NOXAR campaign.

After having smoothed (90 second averaged) data with a 20 point sliding average, oscillations with wavelengths of about half an hour to several hours became apparent. This shows that the night NO measurements were thus clearly not randomly distributed.
as was assumed in expression (4-6). A flight where the photolytic converter was switched off and TR2 thus also measured NO was used to demonstrate that the oscillations appeared both in the signals of TR1 and 2 (Figure 4.6a). Interestingly the instruments thus reacted similarly to some kind of effect which could not be eliminated with the zero (and zeroing) calibrations. Further investigation showed that these oscillations were neither an effect of the newly introduced zero calibration nor of the humidifying unit, since oscillations could also be found on flights from the campaign in 1995-96 (Figure 4.6b) where the zero calibration was not used. However, the difference $S_{\text{diff}}$ of the background-signal obtained in pre-reactor- and measure mode exhibited a striking similarity with the oscillations. As mentioned before, the reason for this signal difference is not known but Drummond et al. [1985] suggested that it might be attributable to different intensities of the interference signals between both modes. (Differential wash-out of interfering substances as a consequence of changing ambient humidity concentrations would then be one possibility to explain the oscillation).

Since $S_{\text{diff}}$ is determined during zeroing calibrations (at 20 minute intervals) it can be used in an empirical correction to reduce noise from the NO measurements. With linear regression the variance of the oscillating signal of TR1 ($S_{M,\text{circ}}$) could be explained by 60% through $S_{\text{diff}}$ for the flight depicted in Figure 4.6a.

$$\hat{S}_{M,\text{circ}} = \alpha \cdot S_{\text{diff}} + \beta \quad (4-7)$$

By subtracting the fitted values $\hat{S}_{M,\text{circ}}$ from the respective measured signals $S_M$, the precision of the 2-minute averaged NO values could be improved from 23 pptv to 8 pptv (Figure 4.6). This value is closer to the theoretical value. Comparison of Figure 4.6a and 4.6c reveals that $S_{M,\text{circ}}$ and $S_{\text{diff}}$ are phase-shifted. With more elaborated statistical techniques this lag could eventually be considered and $r^2$ of expression (4-7) increased, which would further improve precision of the corrected data. If the parameters $\alpha$ and $\beta$ determined during nighttime NO-measurements were applicable to daytime conditions, the precision of these measurements could be improved by inserting the parameters and calibrated values $S_{\text{diff}}$ into expression (4-7). This approach would constitute a more elaborated correction of the daytime NO measurements than the subtraction of an averaged NO offset (termed offset-correction in Figure 4.5) from adjoining nighttime flights, which was adopted at data processing time.

It is concluded that the data submitted to the DLR and NASA Ames archives in May 1998 (and possibly also flights from the first NOXAR campaign in 1995-96) contain non-random noise which makes it impossible to look at effects smaller than the amplitude of the observed oscillation. The size of this artifact has the same order of magni-
tude as the expected concentrations increase downwind of moderately frequented air-
traffic corridors. Emphasis in this thesis will therefore be placed on effects causing
larger signals such as convection and lightning.

\[
\begin{array}{c|c|c|c|c|c|c|c|c}
\text{NO [pptv]} & -50 & -40 & -30 & -20 & -10 & 0 & 10 & 20 & 30 & 40 & 50 \\
\hline
\text{dn/dc [pptv]} & 0.00 & 0.01 & 0.02 & 0.03 & 0.04 & 0.05 & 0.06 & & & & \\
\end{array}
\]

**Figure 4.7.** The histogram with gray bars shows the scatter of the 2-minute averaged NO values of the flight from September 12, 1997. The standard deviation is 23 pptv. The transparent bars on top of it show that the scatter of the data can be reduced with the proposed correction. The standard deviation is 8.3 pptv.

### 4.4.2.2 Accuracy of NO and NO\textsubscript{2} measurements

Systematic errors can occur from a number of sources. The passage of the aircraft could potentially alter the sampled ambient NO\textsubscript{x} concentrations. When air is in the sampling system the NO concentration can be modified by heterogeneous wall reactions and by exchange with cabin air. The first possibility was precluded in section the section on contamination sources where heterogeneous reactions were found to be a minor problem due to the short residence time in the sampling lines [Brunner, 1998]. During long stopovers of the B-747, leak-tests were performed by venting NO gas around all tubes and connectors and this latter error source found to be negligible.

Here it is assumed that systematic errors only originate in the calibration procedures. Calibration gas (6 ppmv NO in N\textsubscript{2}) was filled from a 40 liter bottle to 1 liter cylinders, which then served as the calibration standard in the aircraft [Brunner, 1998; Dias-Lalcaca et al., 1998]. Three small cylinders were rotated over the course of the campaign. These cylinders were calibrated relative to a NO “reference” bottle (about 100 ppmv NO in N\textsubscript{2}) before and after their use in the aircraft. At the end of the campaign
this “reference” bottle was calibrated by Landesanstalt für Umweltschutz (LFU), Germany, and all measurements corrected accordingly by -5%. Since this calibration was in disagreement with other “reference bottles” used by ECO PHYSICS AG, the associated uncertainty was estimated to ±5%. The NO concentrations in the small cylinders were not very stable [Brunner, 1998] and typically decayed by about 0.5-3.5% during the one month operation in the aircraft. The decay is most probably a consequence of the conversion of NO to NO₂ due to oxygen impurities contained in the cylinders but decay could not always be fully explained by the measured NO₂ increase. The evolution of the instrument’s sensitivities (obtained during the span calibration) from both TR1 and TR2 suggest that the NO decay took place linearly in two out of three cylinders. For one cylinder (operational between September 24 and October 26, 1997), however, the sensitivity calibrations suggested an exponential drop of the NO mixing ratio by about 10% within the first three days. This large and rapid decay can hardly be explained by changes in the TRs’ sensitivities. For this case an exponential fit of the $F_{NO}$ values was used and scaled to the calibrated NO decay. The associated error was estimated to be ±5.0% for this case and to ±1.5% for all other cases.

The mass-flow controllers of the Environics S-100 calibration gas-mixing unit were calibrated with a Gilibrator™ Air Flow Calibration System at the end of the campaign. Subsequently the NO concentration of the calibration gas mixed during in-flight sensitivity calibrations was corrected by +7% (±1%). The precision of the in-flight sensitivity calibrations (±0.5%) and the error from the linear interpolation during sensitivity calibrations (±1%) were estimated by [Brunner, 1998].

4.4.3 Overview Uncertainty

It is important to realize that both the precision and accuracy of the NOx analyzers are not constant over the course of time. This has several reasons: The decreasing background signal improves the TRs’ precision with increasing flight time. Moreover, after long ground times such as during Swissair’s A and C-checks, taking place for one and three days respectively on monthly/bi-monthly basis, the instrumental precision slightly decreases. The instrumental artifact presented in section 4.4.2.1 is not constant with time. The compilation of precision and accuracy presented below should be representative for a flight time of at least three to four hours. The NO₂ uncertainty has been determined by Brunner [1998]. Precision (2σ) was estimated to 90 pptv and accuracy of 11%. However, the TR analyzer exhibited a signal difference of 100-200 pptv when the photolytic lamp was switched on and off. The value achieved in practice is therefore worse. NO₂ is therefore only used semi-quantitatively to trace plumes.
Data quality assessment

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<td></td>
<td>Uncertainty in mass-flow controllers</td>
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<tr>
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Table 4.3. Overview uncertainty of NOXAR measurements performed during POLINAT 2 and SONEX.

4.4.4 Possible Contamination sources

Since the NOXAR sampling nozzle is situated at the very back of the aircraft, an alteration of ambient air by the aircraft itself needs to be investigated. Potential chemical contamination sources of ambient air include the following: Exhausts from the engines, cabin air escaping through leaks around windows and doors and exhausts of the cabin’s air-conditioning system. The downward facing engines and the strong directional flow of exhaust gases preclude the first possibility [Brunner, 1998]. Aircraft windows are hold in place by the pressure gradient between cabin air and the about three-fold smaller ambient air pressure at cruising altitude which results in a constant loss of cabin air through this path. Probably an even larger amount of air exists around the heavy doors [Arthur Gachnang, Swissair Technics, personal communication, 1997]. The effect of cabin air, which can contain appreciable levels of NO due to cigarette smoke as well as exhaled air of humans which contains (5-20 ppbv) endogenously produced nitric oxide [Gustafsson et al., 1991 Schilling et al., 1994] therefore needs to be considered. However, the maximum tolerable leak rate of 2000 cubic feet per minute is about a thousand times smaller than the volume of air passing by the sampling system during that same time period of time [Brunner, 1998] and therefore makes contamination from this source very unlikely. Last but not least, the exhaust of the cabin’s air-conditioning system is at the lower end of the aircraft near the wheel box, and aerodynamics therefore makes it impossible to sample output from this source. (Arthur Gachnang, Swissair, personal communication, 1997). The best evidence that aircraft sources are negligible comes from night-NO measurements (see section 4.4.2.1).
On the tropical route between Bombay and Hong-Kong simultaneous spikes of NO, NO₂ and O₃ were occasionally observed, typically when the aircraft crossed the outer edge of a convective ambos. Origin of these spikes is an unsolved problem but a measurement artifact cannot be ruled out [Parrish D., NCAR, personal communication, 1997]. This statement was confirmed from Boeing:

"When the airplane is exposed to precipitation or other particular matter impacting particles deposit a net charge onto the airplane surface due to the triboelectric (frictional charging) effect. The net charge quantity is dependent on temperature, particle density and aircraft speed. Since the capacitance of a large airplane in flight is only about 1000 pF, the potential difference between the airplane and the surrounding space can be as high as 100 kV. This large potential creates an intense electric field around the aircraft, especially around surfaces with sharp edges i.e. wing and empennage tips, blade antennas and other surfaces with sharp edges. Eventually, the electric field around these surfaces will start to ionize the surrounding air and corona discharge will occur. Corona discharges are likely when the airplane is in or near a lightning environment. Since the net charge deposited onto the airplane from a lightning attachment or nearby lightning is orders of magnitude higher than that associated with triboelectric charging, nothing can be done to avoid corona discharges. As the airplane approaches an active lightning cell (thunderstorm) the airplane is affected by the huge potential with the cell. It is very possible for corona discharges to occur on the airplane extremities as well as on the blade antennas and the sample inlet. The charge/discharge waveform is similar to a capacitor curve. The initial charge accumulates until corona occurs then discharges to the point where the corona stops then repeats the cycle. It is important to note that not all the energy is released in a single discharge. The energy of the discharge is related to the current and resistance. The cycle rate is dependent on the charge polarity with positive charge discharging at a slower rate then negative charge. The total time of corona discharge is dependent on how long the airplane is in a severe triboelectric environment which may be milliseconds to hours." [Joe Heeter, Boeing, personal communication, 1998].

Corona discharges are known to produce ozone as well as nitrogen oxides and the measured spikes could therefore be an artifact of the measurement. This hypothesis was tested by handing out questionnaires to the pilots who noted time and duration of the occurrence of silent discharges on cockpit windows. Such discharges are better known under the name of "St. Elmo's Fires" and were reported on a few occasions prior to the observation of aforementioned spikes. Origin of these spikes deserves more investigation. If not found to be an artifact, it would confirm a tentative suggestion of corona produced O₃ and NO₂ enhancements in thunderstorms [Winterrath et al., 1999].
4.5 Field Intercomparisons

The performance of the modified NOXAR system will be compared against measurements from the DLR Falcon and vertical ozone profiles from balloons launched at Payerne, Switzerland.

4.5.1 Intercomparison flight with DLR Falcon

Apart from the data quality studies performed in the laboratory, in-flight instrument intercomparisons are an important test to assess the relative performance of two different measuring systems. An intercomparison flight between the DLR Falcon and the Swissair B-747 was therefore carried out on September 28 in the radar zone of the Shannwick (Ireland) air-traffic control area. The DLR Falcon followed the B-747 for about 15 minutes at a distance of about 1 km. The intercomparison took place in a cloudy environment in the upper troposphere at about 9 km altitude. Since the intercomparison flight took place at the eastern entry point to the NAFC with dense westbound air-traffic, the NOx field was very inhomogeneous even at small scales. The average NO concentration was rather close to the detection limit of the NOXAR instrument (Figure 4.8). As to be expected from daytime chemistry, the NO2 fraction of total NOx was therefore falling below the detection limit of our instrument and could thus not be compared. Both the B-747 and the Falcon encountered several aged aircraft exhaust plumes making the intercomparison fairly difficult to interpret. Nevertheless it could be shown that concentrations sampled by the two instruments were within the combined instrumental errors (see also Ziereis et al., 1998).

Some of the encountered differences can be explained by the different flight patterns: The DLR Falcon flew at constant altitude while the altitude of the B-747 oscillated around the track of constant altitude with an amplitude of 50 ft due to the activated auto-pilot. It is concluded that the conditions for an intercomparison flight were unfavorable but that both the NO and the ozone measurements agreed well within the combined errors. The semi-encounter between the NOXAR B-747 and the SONEX DC-8 on November 09 potentially allows a rough intercomparison of the NOXAR ozone measurements and the DIAL LIDAR of the lower flying DC-8. In addition, the MOZAIC flights during the POLINAT 2 most likely allow intercomparisons between the two different measuring systems.
4.5.2 Intercomparison with Payerne sondes

In Figure 4.11 vertical ozone profiles from NOXAR measurements and Payerne sondes are depicted. No formal intercomparison was performed as during the first NOXAR campaign. However, the graphs suggest that no altitude trend was present anymore with
the PTFE coated ozone absorption tube. In order to be sure, a more formal comparison would have to be performed.

**Figure 4.11.** Ozone concentrations measured during descent into Zurich airport (squares) and Payerne balloons. Thin lines indicate data without laboratory calibration and thick lines data corrected with laboratory calibration. (Note: year in graph should be 1997).
5 Availability of Measurements

In this chapter temporal availability of the NOXAR measurements is first discussed. Spatial availability is examined with respect to stratospheric cruising time. In the last section geographic origin (with respect to altitude) of the sampled air masses is investigated by means of back trajectories started along the flight track.

5.1 Temporal availability

![Figure 5.1. Time diagram presenting an overview of the North Atlantic mission dates of the DLR Falcon, the NASA DC-8 and the Swissair B-747. Dashed lines indicate wing by wing intercomparison flights (Falcon and DC-8) and coordinated flights in the same air mass (Falcon-B-747). The dotted line indicates the coordinated flight between the DC-8 and the B-747. Some gaps in the B-747 North Atlantic measurements can be explained by Far East operations or by extended ground checks of the B-747. F followed by a number indicate respective Falcon flight numbers. The labels T, SNN and BGR stand for test-flight, flight to or out of Shannon, Ireland or Bangor, USA respectively.]

The base airport of the Swissair B-747 airliner is Zürich-Kloten, Switzerland (47°N 8°E), from where the aircraft serves destinations at the Eastern US (Boston, New York, Philadelphia, Atlanta, Chicago)- Atlanta being the most frequently approached destination due to the local hub of code-share partner Delta Airlines. After having followed the organized track system (OTS) in the NAFC the B-747 thus frequently followed a North-South track above the easternmost states of the US continent. Take-off for the westbound flights typically takes place between 0900-1100 UTC and the respective eastbound flights depart at about 2100-2330 UTC.

Campaign dates were from August 13 to November 23, 1997. Thanks to Swissair’s flight operations office’s efforts to coordinate the B-747 North Atlantic operations with the mission days of the DLR Falcon and the NASA DC-8, valuable North Atlantic
Availability of measurements

flight profiles could be obtained during the intensive operation periods of POLINAT 2 and SONEX. The NOXAR system therefore provided data (west- and eastbound) for the following SONEX (S) and Falcon (F) flights: During POLINAT 2 Phase I B-747 flights were carried out on September 27 and 28 to coincide with the DLR Falcon's observations of the enhanced NOx concentrations in a stagnant anticyclone on September 26 (F5) and for the DLR-ETH intercomparison flight on September 28 (F6, F7). During the POLINAT 2 Phase II, the B-747 was operated in the North Atlantic on a daily basis between October 11 and 17. The SONEX Ames to Bangor transit flight (S1) took place on October 13, the Falcon (F8/F9) southbound survey to Tenerife on October 14 and the SONEX (S2) Bangor to Shannon flight in clean air on Oct 15. Due to B-747 Far East operations no coverage could be achieved on the coordinated DLR-NASA westbound flight (F10, S3) on October 18. However, daily B-747 measurements were performed between October 20 and 26. During that time DLR and NASA coordinated a Southern survey on October 20 (S4, F11/F12) and a corridor track crossing on October 23 (S5, F13). During the final transit flight to Oberpfaffenhofen, Germany, the Falcon performed measurements in a stagnant high west of Shannon (F14) while the SONEX team carried out a Northern Survey on October 25 (S6). In order to be able to carry out laboratory calibrations there was a temporary interruption of our measurements which were resumed on November 05, when the DC-8 was stationed in Bangor and carried out a maritime Canada survey flight on the same day (S11). A coordinated flight between the DC-8 and the B-747 was arranged on November 09 during a SONEX cross track survey (S12).

5.2 Spatial availability

5.2.1 Stratospheric Cruising Time

As the B-747 burns fuel it ascends stepwise from an initial cruising level of about 9 km to a flight level of about 11-12.5 km before descending into the destination airport. This leads to a systematic altitude pattern with peak altitudes being reached at the US East coast on westbound flights and over Europe on eastbound flights. Due to the average position of the jet stream in autumn 1997, the westbound flight tracks were shifted by 7 degrees to the North relative to the average position of the eastbound flight tracks. The physical processes and chemical reactions are different in the UT and the LS. For the interpretation of the measurements it is therefore important to distinguish between flight sections carried out in either atmospheric compartment. The relative position of the aircraft with respect to the tropopause (defined here as PV2) can be evaluated using ECMWF fields, which were interpolated in space and time to the B-747 flight tracks. The vertical distance between the B-747 and the tropopause can best be represented by the difference Δθ between the potential temperature at the flight altitude and at the
Temporal availability/Spatial availability

tropopause level. A positive value of $\Delta\theta$ thus indicates flying in the stratosphere. The relative time spent below a given level expressed by $\Delta\theta$ has been calculated at $5^\circ$ intervals between $+5^\circ$ E to $-80^\circ$ E (Figure 5.2) and 35 to 55$^\circ$ N (Figure 5.3).

Figure 5.2. Meridional dependence of sampling time below a given level relative to the tropopause (thick line, representing PV-2 level). On the Y-axis the distance of the aircraft relative to the PV-2 tropopause is measured as the difference in the potential temperature ($\Delta\theta$) between the tropopause altitude and the altitude of the aircraft. Dotted isolines ($\Delta\theta<0$) represent measurement time in the upper troposphere and solid isolines ($\Delta\theta>0$) measurements in the lower stratosphere. The number of (2-minute averaged) measurements in each $5^\circ$ longitude bin is indicated at the top of the graph.

The tropopause altitude between Europe and the United States' east coast exhibits two local maxima (ridges) at $+5^\circ$ E and $-50^\circ$ E and two local minima (upper level troughs) at $0^\circ$ E and $-62^\circ$ E respectively. This structure is important for the interpretation of the measurements: the quite pronounced upper level trough above the US east coast leads to a relatively smaller tropospheric sample size in the period of August to November 1997 in this region. (Note that the representativity of the SONEX flight tracks was biased oppositely since they were optimized to maximize flight time in the troposphere (below PV-2) [Thompson et al., 1999].) During the 1995 NOXAR campaign a similar succession of upper level troughs and ridges, but with a considerably less pronounced amplitude, was observed.

The graph also reveals that the majority of all measurements were taken in a narrow band between $\pm10$ K above and below the tropopause. It can be seen that hardly any
flight took place at altitudes higher than +40 K above the tropopause, which, assuming the US standard atmosphere, is equivalent to a distance of only about 2.5 km above the tropopause. Figure 5.3 illustrates the strong latitudinal dependence of the tropopause altitude. At 35° N only about 10% of all measurements were performed above the PV2 level, while at 55° N half the number of all measurements are performed in the UT and the LS respectively.

(The criterion to determine the tropopause altitude is somewhat controversial. If it were chosen to be the PV4 level, the tropopause would approximately follow the curve with Δθ=+5K.) It can be concluded that on a meridional average the stratospheric cruising time on the North Atlantic route was close 50% with exceptions during crossing of upper level troughs and ridges.

5.2.2 Origin of sampled air masses

While statistics of the stratospheric cruising time along the flight track are useful, it is also important to look at statistics of the history of the sampled air masses. The analysis was performed by passing all trajectories (see section 6.2.1) starting along the POLINAT 2 and NOXAR flight tracks, through a 3D-grid (horizontal resolution 1x1 degrees, vertical resolution 1 km) and increasing the counter of a grid cell when crossed by a trajectory. Only trajectories from measurements performed at cruising altitude (defined here as pressure< 400 hPa) were considered to allow for detection of (synoptic...
scale) vertical ascent from lower atmospheric levels. The result of this analysis is presented in Figure 5.4, which shows a histogram of the altitude distribution of all counts.

![Figure 5.4](image)

**Figure 5.4.** Normalized histograms of the altitude distribution of air-parcels along the five-day back trajectories started along all NOXAR (1995/1996) and POLINAT 2 (1997) flight tracks. Along each trajectory 121 one-hour steps are performed, leading to a total number of 2.2 (JJA 1995), 2.9 (SON 1995), 1.9 (DJF 1995/1996), 2.5 (MAM 1996) and 1.5 (SON 1997) million counts. The shaded area covers the altitude range between the lowest level from which trajectories were started and the flight top altitude of 12 km. Solid lines indicate the entire 5 day history and dotted lines visualize the same result with an exponential decay factor of one day.

It can be seen that 75% of all air masses observed at cruising altitude were constrained to a relatively thin band between 2.5 km above and below the mean cruising level of 10 km during the previous five days. Since only trajectories starting at 400 hPa (about 7 km) or higher were considered, all counts (6%) from lower levels can be explained with (synoptic) ascending motion. The top flight level of the B-747 is about 12 km and was only rarely reached, when the aircraft was not fully loaded. Only a small fraction (<3%) of all counts were recorded above that level. Figure 5.4 shows that the majority of these counts occurred on the tropical route between Bombay and Hong-Kong, where the tropopause is much higher so that downward transport to the aircraft’s cruising altitudes still occurred within the troposphere.

No back-trajectory (starting along the aircraft flight track) ever descended from altitudes higher than 17 km during the previous five days. This implies that using a commercially operated B-747 airliner only air from troposphere and the lowermost stratosphere [Holton, 1992] can be sampled. The strong ozone enhancements in higher
stratospheric layers can be used to test whether this hypothesis is true. The 99% percentiles of the sampled ozone concentrations of 467 ppbv for NOXAR (between 1995 and 1996) and 350 ppbv for POLINAT 2 are significantly smaller than ozone concentrations from higher levels.

Interestingly the vertical distribution of the air mass history does not exhibit a significant seasonal cycle. This may be expected for the stratosphere, where the strong stratification prevents (net) vertical mixing throughout the year. However, one might expect higher seasonal variability at lower levels in the troposphere due to the seasonal variability of the predominant weather patterns.
6 Tools for Source Attributions of NOx

In this section the tools are introduced which are used for the interpretation of the measurements (see sections 7 and 8). For the interpretation of NOXAR data external data are used which are described in section 6.1. The tools themselves are described in the subsequent section (6.2).

6.1 External Data Sources

6.1.1 ECMWF fields

Meteorological fields from the European Center for Medium-range Weather Forecast (ECMWF) are used throughout this work. We used analyzed fields at a resolution of T213L31 (i.e. 213 spectral components, corresponding in midlatitudes to a horizontal resolution of about 0.7 degrees on 31 vertical levels) with a temporal separation of six hours. We also interpolated standard model parameters in space and time along the flight track. In addition potential vorticity (PV $[1 \text{ PVU} = 10^9 \text{m}^2 \text{s}^{-1} \text{Kg}^{-1}]$), a dynamic tracer for stratospheric air, was calculated. Wind and temperature from the model were compared to the (2-minute averaged) measurements from the standard B-747 sensors and in general very good agreement was found. The East wind component (Figure 6.1a) had a positive mean value of about 20 m/s and the strongest wind speeds exceeded 90 m/s on eastbound flights when pilots used the jet-stream to conserve fuel. The temperature values of the model and the measurements (Figure 6.1c) agreed reasonably well. However, since the tropopause altitude may vary quite significantly over the course of a six-hour period, the largest differences between the measurement and the model output occurred close to the tropopause. The good agreement between measured values and model output thus gives greater confidence for using these fields for synoptic scale analysis of air motion and thus calculating back trajectories.
Figure 6.1. Scatter plot of ECMWF fields interpolated in space and time along the NOXAR flight track versus the meteorological measurements (2 minute averages) from the B-747's standard sensors. All flights between Zurich and the United States which were performed between August 13 and November 23, 1997 are considered.
6.1.2 Cloud imagery

Satellite imagery from the GOES-8 geostationary satellite was used to establish the location and horizontal extent of convective systems, as well as the cloud top temperature. Given the transience of convection, where systems can change significantly in a few hours time, it is necessary to use geostationary imagery with a time resolution of 1-3 hours, instead of the better calibrated instrumentation on the NOAA polar orbiting satellites (where imagery is typically only available twice per day). Even so, brightness temperatures of the geostationary satellites are probably good to 2K. This is confirmed by comparisons of in situ tropical upper tropospheric temperature measurements made by aircraft with brightness temperatures from the GMS Japanese geostationary satellite made during the Stratosphere-Troposphere Exchange Project Experiment in early 1987 [Russell et al., 1993].

For this study, only the infrared window channel was used (Channel 4, 10.5 to 11.5 microns) with a spatial resolution of about 10 km. Cloud altitudes were established by a simple comparison of channel 4 brightness temperature to analysis temperatures. Though this scheme will yield substantial underestimates of cloud altitude for optically thin clouds, it is probably quite accurate (to the accuracy of the analysis temperatures and the brightness temperatures) for deep convection. In fact, very few clouds have brightness temperatures cold enough to match the cold temperatures of the upper troposphere (~200 mb) where the long-range NOXAR aircraft were flying. Thus, it is unlikely that any high thin cirrus would be mistaken for convection reaching these aircraft altitudes. If anything, this simple method probably underestimates the extent of convective cloudiness reaching aircraft altitudes, mostly by underestimating the cloud altitudes of the anvil edges of convective systems.

6.1.3 Lightning observations

We used both data from the U.S. National Lightning detection network (NLDN) [Wacker and Orville, 1999] and from the Optical Transient Detector Satellite (OTD) [Christian et al., 1996] to explore the history of lightning encounters of plume air masses. The NLDN provides lightning data covering the continental United States and the adjacent coastal areas (20°N-53°N and 60°W-130°W) from an array of more than 100 sensors detecting ionospherically propagated electromagnetic signals from cloud-to-ground (CG) lightning discharges. Recent assessments showed that for our application the system has a very high median location accuracy of 500 m. The expected flash detection efficiency for continental thunderstorms ranges from 80% to 90% for those events with peak currents above 5 kA, varying slightly by region [Cummins et al., 1998; Idone et al., 1998]. Although the detectors are positioned on the North American continent, the data of this system are also processed to detect lightning occurring at sea.
However, the detection efficiency of this long-range network decreases strongly with increasing distance from the shore. By comparing observations from different locations within the U.S. arrays and by carrying out joint trans-Atlantic experiments involving sensors from Meteo France, \textit{Cramer and Cummins} [1998] showed that for the observations of several marine thunderstorms, the detection efficiency was about 20% at local night but dropped to only a few percent during local day time. An evaluation of the detection efficiency of the NLDN's long range channel as a function of local zenith angle and distance from the shore is currently under way at the Global Hydrology and Climate Center of the NASA MSFC (\textit{Dennis J. Boccippio}, personal communication, 1999).

For lightning occurring in remote areas, such as the mid North Atlantic, it is necessary to use satellite observations. The OTD satellite has been continuously monitoring global intracloud (IC) and CG flashes from a near-polar orbit since April 1995. The OTD sensor attitude (orientation) may rotate over the course of an orbit, with individual geographic locations experiencing strongly varying view periods between 1 and 270 seconds which makes it necessary to correct climatologies for viewing time. Lightning can be detected with an efficiency of about 55 to 70% [\textit{Boccippio et al.}, 1999]. Comparisons of simultaneous space borne and ground based lightning observations revealed that the IC:CG ratio can vary considerably across the United States [\textit{Boccippio et al.}, submitted 2000]. This observation is discussed in more detail in 8.2.2 and 8.2.3 and a graphical representation can be found in Figure 6.2.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ic_cg_ratio_map.png}
\caption{Graphical representation of the IC:CG ratio in the U.S. (courtesy Dennis Boccippio, NASA Marshall Space Flight Center).}
\end{figure}
6.1.4 ANCAT data base

The ANCAT/EC-2 worldwide air-traffic emissions database of the year 1991 [Gardner et al., 1998] was used at 1x1 degree horizontal and 1 km vertical resolution. Since the amount of trans-Atlantic air-traffic varies over the course of a year, the database contains emissions for four representative months. The best temporal match with the POLINAT 2 and SONEX campaigns is achieved by using the October sub-set of the database, for which global total emissions amount to 0.131 Tg NO₂. Note that the data bank is based on optimum flight profiles and flight tracks (great circles) and does not take into account any Air Traffic Control (ATC) delays. Neither does it include a diurnal air-traffic cycle nor account for day-to-day North-South shifting of the entire corridor, which optimizes flight tracks relative to the position of the jet stream.

6.2 Methods used

6.2.1 Kinematic trajectories

The ECMWF fields described in section 2.2 were the basis for calculating three-dimensional kinematic back trajectories for all POLINAT 2 flights with the software package “Lagranto” [Wernli and Davies, 1997]. The trajectories were started at the whole hour closest to the measurement time and calculated with an integration time step of 30 minutes. They are used in all applications presented below to identify the history of air masses as well as to uncover exposures to convective clouds, lightning flashes and aircraft emissions.

6.2.2 Tracing along the trajectories

Trajectories are well suited to investigate the geographic origin of an air mass. However, due to the limited resolution of the model, sub-grid processes are not considered:

- Gravity wave breaking
- Clear Air Turbulence
- Convective up-and downdrafts

No simple solution exists for incorporating the first two points. However, Brunner et al. [1998] have overlaid animated (infrared) satellite images on trajectories to identify frontal systems and convectively active regions. This process can be automated to scan large data sets for identifying convective encounters and will be labeled “tracing along trajectories”. Several diagnostic tools based upon output from numerical weather prediction and satellite observations have been used and are described in the following subsections. Since these tools can be automated relatively easily, they can be applied to large numbers of flights (such as from NOXAR or MOZAIC (Measurements of OZone and water vapor by Airbus In-flight aircraft).
6.2.2.1 Tracing convective influence

For every time-step along a given back trajectory, the cloud top height from the corresponding infrared image is determined. By plotting it against time (history of the air mass), a vertical section of the cloud-top height along the trajectory is obtained (see Figures 7.10 and 7.16). As a first order approximation, convective influence is said to have occurred, when the trajectory's history shows encounters where the (satellite derived) cloud top temperature was smaller than that of the trajectory altitude [Jeker et al., 1998; Thompson et al., 1999]. Despite the ease with which this algorithm can be automated and applied to large sets of trajectories, the following issues may potentially compromise the results:

- Convective clouds with active vertical transport are treated in the same way as inactive clouds. In order to only pick active clouds (in selected case-studies), computer animations were created showing the movement of the air masses along their calculated 5-day back trajectories, which are plotted over corresponding infrared satellite images. For bundles of coherent trajectories activity of a cloud was visually examined.

- High altitude cirrus clouds can have low brightness temperatures similar to convective clouds, leading to an overprediction of convection in the brightness temperature-tracing scheme. For selected case studies cirrus clouds were visually identified in computer animations and affected trajectories were excluded from the analysis.

- As noted in section 2.3, the determination of the brightness temperature is based upon radiative emission from the cloud-top and an optically thick cloud is assumed. At the edges of anvils, however, the clouds may be less optically dense. Infrared radiation from lower cloud levels or from the ground may also reach the satellite, which detects a seemingly higher cloud temperature. This effect is particularly pronounced over warm surfaces such as the Gulf Stream or the continents in the warm seasons. The altitude of the cloud is therefore underestimated at the edges of an anvil and so is convective influence. This effect was compensated for by allowing a convective cloud to be 5 degrees warmer (chosen based upon experience) than the crossing trajectory.

6.2.2.2 Tracing lightning influence

Analogous to the „brightness temperature tracing“ described in the previous section, lightning activity in the trajectories' vicinity was automatically traced. For every time step along a trajectory the number of lightning flashes in the trajectory's vicinity was
obtained and accumulated lightning flashes for the entire trajectory determined. The latter number includes an exponential decay factor, which gives earlier events less weight. The factor also allows for sub-scale-mixing processes (e.g. eddy diffusion) along the trajectories, for uncertainties in trajectories increasing with time and for chemical sinks that were not simulated explicitly.

One uncertainty in the tracing technique is that, depending on intensity of a convective encounter, the trajectory may become unreliable. A concept of “most recent convection” was therefore adopted and lightning counting stopped after the first period of on-going lightning strikes (which can last a few time steps). It turned out, however, that the results did not show much sensitivity to adoption or neglect of this concept.

An important point to note is, that only cloud-to-ground (CG) flashes are captured in the NLDN whereas Intracloud (IC) flashes remain largely undetected, which leads to an underestimate of the total number of flashes affecting an air mass. IC flashes are detected by the OTD satellite. Because the orbiting platform only observes an area of interest for short periods of time, OTD information can therefore not be included in the lightning tracing approach, where continuous monitoring of the lightning field is required. Both the ratio of IC to CG flashes and the NO\textsubscript{x} production per flash of each type are still a field of active research [Gallardo and Cooray, 1996; Price et al., 1997; DeCaria et al., in press] with published values widely differing. Only CG flashes were considered in the lightning tracing procedure, but the potential impact of this simplification is discussed in section 7.1.

### 6.2.2.3 Tracing aircraft influence

The release of nitrogen oxides by jet-aircraft is followed by a series of complex mixing events until the emissions are finally dispersed in the atmosphere. For modern jet-aircraft the atmospheric dispersion regime is reached after approximately three hours when the original emissions are diluted to the ppbv level [Schumann et al., 1998]. The crossing of such plumes results in sharp spikes in the NO measurements [Schlager et al., 1997] which for NOXAR have been manually marked by Brunner [1998]. In this work we detected them with an automatic algorithm. However, older emissions are not discernible and counting of spikes therefore leads to an underestimate of the importance of air-traffic. Such older emissions can be roughly estimated with the following approach:

Estimates of the NO\textsubscript{x} concentration increase (Dominik Brunner, KNMI, personal communication, 1998), which can be attributed to aircraft emissions, were made by combining the information from backward trajectories with the data of the 3D aircraft emission database ANCAT/EC-2. The ANCAT emission rates in each grid box, given as mass emitted per time, were converted into emission rates in terms of volume mixing.
ratio increase per time. (For this conversion, the volume and air mass of each grid cell had to be calculated. The air density as a function of altitude was assumed according to the ICAO standard atmosphere.) These emissions are summed along the 5-day trajectories with a 3D linear interpolation of the concentrations between grid box centers. An artificial lifetime of NOx (5d, 10d, $\infty$) was introduced to reduce the weight of older emissions. The results were neither very sensitive to a variation of the lifetime nor to using the same inventory at a 2.5x2.5 degree resolution.

For the first hours until aircraft spikes are sufficiently mixed with background, they are both accounted for by the detection from the aircraft signal and from the ANCAT tracing method. Although this may lead to some overestimate, we do not find this to be a serious problem in the context of this study.

6.2.3 Convective influence plots

For flight planning during SONEX, forecasts of convective and lightning influence were used extensively in the field [Thompson et al., 1999]. Similar to the tools described in the pervious two paragraphs, these analyses were based upon a combination of both convective and lightning influence analysis. By starting trajectories from a 1 by 1 degree grid of starting points, a map of the area affected by convection and lightning can be obtained (see Figure 7.2). The difference between these products and the tools described in the previous two paragraphs are the analysis fields (GSFC ASM (GEOS-1) instead of ECMWF), and type of trajectories (isentropic instead of kinematic).
7 Selected Case Studies

7.1 Frontal activity over the Eastern United States

A series of large NOx plumes was observed during four flights to and from the U.S. east coast between September 11 and 13, 1997. Early on September 10 the upper-level flow structure was characterized by an elongated PV streamer that moved slowly towards the eastern part of the North American continent over a region characterized by a moderate north-south temperature gradient in the lower troposphere. Only a weak surface cyclone formed near the leading edge of the streamer and reached the eastern part of the Great Lakes at 1200 UTC on September 11 (Figure 7.1). The PV streamer induced strong low-level northerly flow of warm moist air along its eastern flank and triggered convection just west of the east coast of the United States.

Figure 7.1. Formation of a weak surface cyclone at the U.S. east coast on September 11. Thin lines indicate the 900 hPa potential temperature contours (contour interval 2 K). Bold lines symbolize the 900 hPa geopotential height (contour interval 30 m). The shaded area indicates the region where the potential vorticity (PV) exceeds 2 PVU on the 335 K isentropic surface.
In Figure 7.2 the convective influence maps from section 3.4 are applied to interpret the observed NOx concentrations. It can be seen that the highest NO and NO2 concentrations were observed at the U.S. east coast on the NOXAR west- and eastbound flights respectively, on September 11 (Figure 7.2a). The maps of convective influence clearly distinguish the area without convective influence (black) from the convective outflow (colored) from the above mentioned frontal system, which is in good qualitative agreement with the measured concentrations. Note that the easternmost extension of the plumes was observed further off the coast on the flight to Europe. Commercial airliners try to make use of the jet stream on their eastbound passage in order to shorten transit times. In this case the stronger winds can vent the plumes further offshore.

One day later (Figure 7.2b) another, less pronounced NO plume was encountered between 50 and 70° W. Note that the sharp concentration drop at the western edge of the plume is well represented in the map and that the plume’s eastward extension is slightly underestimated. As mentioned above, only convection accompanied by lightning is included in the maps. Underprediction might be explained by vertical transport of polluted continental planetary boundary layer air in clouds, which did not exhibit lightning activity. The map for September 13 (Figure 7.2c) shows that the influence of the frontal system stretched even further out into the Atlantic on that day, which led to
Frontal activity over the eastern United States

Sampling of enhanced NO concentrations between 40 and 70° W, although the enhancement was less pronounced than on the previous days.

**Figure 7.3.** Box plot comparing NO samples performed between September 11 and 13, 1997 with (left part in graph) and without (right part) a convective encounter during the previous 5 days (as determined from the maps of convective influence in Figure 7.2). Horizontal white lines indicate median values, notches the confidence intervals of the medians and thin horizontal lines outliers. For boxes with "no AC" (AC=aircraft) markers, both the short spikes (in the measurements) and the accumulated AC emissions obtained by the ANCAT tracing method were subtracted from the NO measurements (assuming a NOX residence time of 10 days). The "AC" marker indicates all measurements without "aircraft-filtering".

In Figure 7.3, a more quantitative approach is presented to demonstrate the method's ability to automatically separate air masses with and without a history of recent convection. The confidence intervals (notches in the box-plots) of the median values of the data sets with and without convective history do not overlap, which portrays a statistically significant difference in the medians between the two groups. It is thus possible to reliably detect the location of convectively influenced air masses with an automated algorithm. However, there is a significant scatter of the NOX measurements in the case of a recent convective encounter. (This can be explained by different exposures to continental pollution and lightning discharges and to different times at which the NOX loading took place.) With the ANCAT tracing approach we obtained rough estimates of the aircraft influence along the flight tracks and in Figure 7.3 we set it in relation to the scatter caused by the combined effects of convection and lightning. Downwind of convective events, it might therefore be difficult to assess the aircraft NOX increase without additional tracers. Such large heterogeneity in the NOX field has already been observed in model results by Flatøy and Hov [1997] who suggested that
NOx emissions from lightning may cause a variability in free tropospheric composition, making it difficult to distinguish the importance of other sources of free tropospheric NOx without modeling studies where individual sources can be switched on and off. Here we explain the scatter in the NO data with a lightning tracing analysis. Thunderstorms embedded in the frontal system exhibited high lightning frequencies between the U.S. east coast and 250 km offshore. Prior to that, lightning influence on the trajectories occurred over the Gulf of Mexico. (Due to the proximity to the U.S. continent, the NLDN detection efficiency should be fairly good.)

![Figure 7.4](image)

**Figure 7.4.** The upper panel shows 2-minute averaged NO2 measurements on NOXAR eastbound of September 11. An extended plume can be observed between 75°W and 55°W, in tropospheric air characterized by low PV values (dotted line). The lower panel shows the number of accumulated CG flashes (obtained from the lightning tracing method) along the same flight.

The upper panel of Figure 7.4 shows an extended NO2 plume between 75°W and 55°W, in tropospheric air characterized by low PV values. The panel below shows the number of accumulated CG flashes.
Figure 7.5 Linear regression of measured NO\textsubscript{x} from NO\textsubscript{XAR} westbound and eastbound of September 11 versus number of accumulated lightning flashes. Data from westbound flight (measured NO\textsubscript{x}\textsuperscript{*}=NO+NO\textsubscript{2}\textsubscript{ps}) are denoted with solid dots ($r^2=0.64$), and data from the eastbound flight (measured NO\textsubscript{x}=NO\textsubscript{2}) are shown with empty dots ($r^2=0.83$). Note the similar slopes on the west- and eastbound flights of September 11, 1997. (Overall regression with data from both flights yields $r^2=0.72$, fit not shown.)

Figure 7.5 shows that the accumulated number of recent flashes correlates well ($r^2=0.72$) with the measured NO\textsubscript{x}\textsuperscript{*} (=NO+NO\textsubscript{2}ps) concentrations on the westbound flight (filled dots), and the NO\textsubscript{x} (=NO\textsubscript{2}) concentrations measured on the eastbound flight (empty dots).

By performing a linear regression with the data from both flights, the following relationship is obtained:

$$\text{NO}_x = a \times (# \text{ CG-flashes}) + b,$$

where NO\textsubscript{x} is the measured (2 minute averaged) NO\textsubscript{x}\textsuperscript{*} concentration in pptv, $a=0.416$ [pptv/CG-flash] the slope and $b=204$ [pptv] the intercept. Note that a regression applied separately to each individual flight, results in about the same slopes but the regression of the eastbound flight ($r^2=0.64$) shows an offset of about 120 pptv with respect to the one from the westbound flight ($r^2=0.83$). This may be explained by the aforementioned difficulty in the NO\textsubscript{2} measurement on this (nighttime) flight. The slope
variables within a factor of about 2.5 when the “viewing area” around the trajectories is altered. In order to reduce arbitrariness we maximized the correlation coefficient $r$. $r^2$ remains below values of 0.3 for squares with side lengths up to about 100 km but significantly increases at a size of 160 km and peaks at 300 km, which is the size used to obtain formula 1. At larger squares the correlation coefficient slowly decreases. For this frontal system squares of 300x300 km (around individual trajectories) represent a rather plausible “viewing area” since lightning flashes were observed in a band of about 300 km West-East extension. When the viewing area is further increased, other thunderstorms, with probably little influence on the air masses are counted and the correlation coefficient thus decreases again. The same procedure was applied to the decay factor, which gives previous lightning flashes less weight. The best fit was obtained with a $1/e$ decay factor of 1 day. This is much smaller than the expected NO$_x$ lifetime at these altitudes and may be caused by mixing, trajectory errors or both.

For the September 12 flight, the analysis shows a significant (2.5 degree) lag between measured NO values and accumulated CG lightning flashes. Moreover a correlation of the same kind could only be observed when the lightning tracing is performed at 6 hours rather than 1-hour steps. This points to possible inaccuracies in the ECWMF fields and/or trajectory errors. On September 13, the measured NO enhancement was too weak for obtaining a good correlation with the accumulated CG lightning flashes. The rather good correlation between CG lightning flashes and measured NO$_x$ concentrations on the September 11 flights has two important implications:

1) Lightning most probably was an important contributor to the large scale NO$_x$ plumes observed both on the west- and the eastbound flights of September 11.

2) A correlation can even be seen one or two days after the assumed NO$_x$ production took place. We therefore suggest that strong mixing processes in the thunderstorms rapidly reduced the initially strong variability of the NO$_x$ field. (Stith et al. [1999] reported sharp NO spikes up to 19 ppbv in the proximity of an anvil). But after this initial regime, the structure of the NO$_x$ plume was conserved rather well until it was sampled by the B-747.

Note that Allen et al. [1999] show a strong relationship between observed lightning flash rate and cloud mass flux in a global transport model based on assimilated winds. Although correlation (1) strongly suggests lightning as a major contributor for the observed NO$_x$ enhancements, the apparent CG flashes could also indicate injection of pollution from the boundary layer, which can easily contain 1-2 ppbv NO$_x$ even in rural
areas of the eastern U.S. Without tracers of anthropogenic pollution, the correlation can therefore not unambiguously prove the lightning origin of the observed NOx plume.

### 7.2 Lightning activity over the Gulf Stream

For cases of marine convection, the vertical transport of anthropogenic NOx is of lesser importance, which gives the lightning contribution more weight for the regional NOx budget at cruising altitude. We found such a situation on November 9, 1997 when SONEX performed the first cross-corridor measurements out of Bangor Maine; NOXAR was operated between Zurich and Atlanta that day.

![Figure 7.6](image)

**Figure 7.6.** (a) Flight Tracks (bold lines) of NOXAR (B-747 symbol) and SONEX (perpendicular to NOXAR westbound flight track) of November 9/10, 1997. NO concentrations in excess of 1000 pptv are symbolized with black squares. "Low" indicates air with low NO concentrations. Numbers mark highest NOx concentrations (1: NOXAR westbound, 2: SONEX, 3: NOXAR eastbound). Back trajectories starting in NOXAR (westbound) NO plume are represented with thin lines and cross an area of intense lightning flashes (C). (Lightning contours are given for 2100-2300 UTC on November 8). Section B marks warm Gulf Stream current, A the cold continent. (b) Shaded area marks stratosphere. Dashed-dotted lines indicate PV-2 (lower line) and PV-4 level (upper line).

A horizontal and vertical section of all flights is given in Figures 7.6a and b, respectively. The measurements were performed downwind of a well developed frontal system resulting from a classical, although moderate case of east coast cyclogenesis taking place between November 7 and 10. An elongated zone of strong baroclinicity extended zonally from Florida to the central Atlantic at 1200 UTC on November 7. A surface cyclone formed below the leading edge of an almost circular positive upper level PV-anomaly at that time. The cyclone intensified and established a T-bone frontal structure (Figures 7.7 and 7.8) where the temperature contrast associated with the warm front was much stronger than for the cold front.
Figure 7.7. Elongated zone of strong baroclinicity between Florida and the central Atlantic on November 9, 1997 at 1200 UTC. The track of NOXAR westbound is symbolized with “O” in areas where NO concentrations were smaller than 1000 pptv and with “X” where they exceeded this level. (Flight level corresponds approximately to the 327 K isentropic level.)

Figure 7.8. GOES-8 image from 2145 UTC on November 8, 1997. The white rectangle encloses a band of high reaching convective clouds (black) which exhibited very strong lightning activity between 2000 UTC on November 8 and 0500 UTC on November 9. Triangles symbolize the location of air masses from the first sub-plume (I in Figure 7.9) and boxes air from the (more prominent) second sub-plume (II in Figure 7.9) at the time of the satellite picture.
Until shortly before reaching the U.S. east coast, the NOXAR westbound flight took place in the lower stratosphere in clean air masses of polar origin, where background NO concentrations of about 100 pptv were sampled (marker "Low" in Figures 7.6 a and b) and a brightness tracing analysis revealed that these air masses were not recently exposed to convection. At about 40°W the aircraft entered the troposphere, which can be seen by a drop in the ozone concentration from 120 ppbv to 70 ppbv (not shown, instead refer to PV-2 surface in Figures 7.6 and 7.7). Only about ten degrees further east, the outer edge of a prominent NO plume was entered at 1445 UTC, where elevated concentrations were measured until 1800 UTC (sections I-III in Figure 7.9).

Figure 7.9. NO measurements from SONEX (thick, dark gray line, 2), NOXAR B-747 westbound flight (thin black line, 3) performed on November 9, 1997. The NOXAR NO concentration enhancement can be subdivided into three sub-plumes marked with I to III. On the respective eastbound flight at night, the B-747 detected very elevated NO\textsubscript{2} concentrations (thin, light gray line, 1) downwind of the area where SONEX detected the highly elevated NO and NO\textsubscript{2} concentrations.

Figure 7.9 shows that the SONEX aircraft, which started sampling the same area with a time lag of about one hour, also detected highly variable NO concentrations with maxima of up to 3000 pptv between 1800 and 2100 UTC. The most prominent NO enhancements were constrained to the cross-corridor flight legs (marker 2 in Figures 7.6 and 7.9) at altitudes higher than 8.5 km between 53.5 and 57°W (section 2 in Figures 7.6a and b). On the respective eastbound flight at night (about 0300 UTC) the NOXAR aircraft sampled NO\textsubscript{2} concentrations in excess of 3000 pptv downwind of the area where SONEX detected the highly variable NO concentrations (marker 3 in Figures 7.6 and 7.9).
Selected case studies

Figure 7.6a shows that the back trajectories starting on flight legs where observations of high NO\textsubscript{x} concentrations were made (on all three flights), followed an upper level trough associated with a surface low-pressure system. This is a rather typical flow pattern, downwind of which numerous NO\textsubscript{x} plumes were sampled during NOXAR [Brunner et al., 1998; Jeker et al., 1998] and on SONEX flights 10 (October 29) and 12 (November 3) [Pickering et al., 1999; Thompson et al., 1999]. During passage over warm Gulf Stream waters with sea surface temperatures of 20-25°C (section B in Figures 7.6a and 7.10, the back trajectories intersected an area of active thunderstorms, which exhibited more than 1900 CG flashes in the highlighted area between 2100 and 2300 UTC on November 8. (Recall that this uncorrected value is a lower limit due to the detection efficiency problems mentioned in section 2.4). Superposition of lightning data on GOES-8 satellite brightness temperatures, revealed good spatial and temporal agreement between the highest convective cells and clusters with the most intense lightning activity.

A more detailed discussion of the structure and history of the NOXAR westbound NO\textsubscript{x} plume suggests that large fractions of the NO enhancements are due to lightning activity as will be shown: The entire plume, which was observed in the longitude range of 50 to 67°W, can be subdivided into three sub-plumes (I to III in Figure 7.9) with marked concentration gradients at about 57°W and 61°W.

![Figure 7.10. GOES-8 derived top temperatures (crosses) and temperatures along the ECMWF back trajectories (diamonds) starting inside first NOXAR sub-plume (1445 and 1515 UTC) on November 9, 1997. GOES-8 temperatures reveal three regimes: In A the trajectories are over the comparatively cold U.S. continent, in B over the warm Gulf Stream Current, in C they cross a region of intense convective activity reaching to the altitude of the trajectories.](image-url)
Lightning activity over the gulf stream

The back trajectories starting in the first sub-plume (amplitude ~600 pptv) experienced significant convective influence for the last time between 15 to 20 hours prior to the measurements. Interestingly, some of the relevant thunderstorms, (not accompanied by lightning activity), developed over the polluted continental area between Boston and Philadelphia (not shown) which apparently did not cause very strong NO concentration enhancements at cruising altitude. Prior to that, some trajectories crossed isolated convective clouds at sea which exhibited low lightning frequencies. The concentrations during the second and most prominent sub-plume reached levels of up to 3000 pptv (section II in Figure 7.9), when the aircraft flew over the wider area of Newfoundland between about 1515 and 1545 UTC. The corresponding back trajectories crossed Nova Scotia, passed southward through the Gulf of Maine and experienced last convective encounters at sea, about 11 hours prior to the plume observation. The air mass moved further South and at -18 hours it was fully immersed in a cluster of convective clouds (squares in Figure 7.8), all of which exhibited very strong lightning activity. The southernmost trajectories left the cloud cluster again at about -21 hours and no convective influence occurred prior to -27 hours before the plume observation was made. On average, these air masses with higher NO content were exposed to stronger and longer periods with intense lightning activity than the air masses sampled during the first sub-plume.

Figure 7.11. The upper panel (a) indicates the number of accumulated CG lightning flashes encountered by the back trajectories during the most recent convective encounter (source L. Pfister, NASA Ames). The lower panel (b) shows NO measurements on the NOXAR westbound flight of November 9. (Data in both panels are averaged at intervals of 1.5 degrees along the flight-track).
Selected case studies

Figure 7.11 shows that a lightning tracing analysis with the model products by Thompson et al. [submitted] revealed a very good proportionality between the accumulated number of lightning flashes and the measured NO concentrations on NOXAR westbound. This suggests that lightning was a major contributor to the NO enhancement. A spatial lag of about 1 degree between measured NO concentration and accumulated lightning flashes can most probably be attributed to inaccuracies in the relatively coarse GSFC ASM (GEOS-1) wind fields (grid-size: 2.5x2.5 degrees) and to gridding of the measured data and accumulated lightning flashes in Figure 7.11. Due to the detection efficiency problems of the long range network, the number of accumulated lightning flashes should be used semi quantitatively and in contrast to the first case-study and no attempt is made to correlate measurements to accumulated flashes to obtain a quantitative relationship.

Note, however, that a lightning tracing analysis using ECMWF instead of ASM wind fields and hourly instead of 3 hourly lightning fields, could reproduce three different sub-plumes but not show a proportionality to the measured NO concentrations. This could be due to differences between the two schemes (see sections 3.2 to 3.4). Furthermore neither approach accounts for the (largely unknown) diurnal variation of the detection efficiency of the NLDN long-range channel. Small location errors in the trajectories have a particularly pronounced effect at times when there are strong changes in the detection efficiency. Different integration times used in both schemes might therefore lead to differences in accumulated lightning flashes.

To further strengthen evidence for the lightning hypothesis, we started ECMWF back trajectories from a 1x1 degree grid at different pressure levels (400, 600, 800, 900 hPa) covering the area between 65 to 75°W and 30 to 45°N to test whether polluted low level continental outflow could have been lifted to the altitude of our trajectories of interest in the marine convective systems described above.

For the three upper levels, we find no evidence of such motion (Figure 7.12 shows representative trajectories at 800hPa) although for the 900 hPa level there are a few trajectories where the air crossed the polluted U.S. continent in the period of 1.5 to 3 days before convection occurred over the ocean. Due to the very short lifetime of NOx at these low levels [Jaeglé et al., 1998], we believe that by the time polluted continental outflow had reached the bases of the convective clouds, large fractions of the initial NOx concentrations must have decayed.
Figure 7.12. 3.5 day ECMWF back trajectories started along 70°W (location of convection and lightning activity) on the 800 hPa surface at 0000 UTC on November 9, 1997. Crosses mark 24-hour intervals along the trajectories. Note that the two air masses, which merge at the cold front, do not originate from the polluted U.S. planetary boundary layer.

This is in line with Crawford et al. (manuscript under preparation) who note that on some sections on that day's SONEX flight track, NO correlates with several hydrocarbon species (e.g., CH₄, C₂H₂, C₃H₈, and butane), although the slope is small. This opens the possibility for convection of moderate amounts of surface NOₓ in the frontal system but the contribution for the SONEX flight should be small and cannot come close to explaining the observed NO mixing ratios of 2-3 ppbv (see also Snow et al. [submitted]). Allen et al. [1999] found, based upon tracer simulations, that this SONEX flight was the one most dominated by the lightning source (at least half of total NOₓ).

We conclude that warm Gulf Stream sea surface temperatures of 20-25°C together with the approaching synoptic-scale disturbance played an important role in triggering convective clouds and lightning discharges, which led to large NOₓ concentration near the tropopause. These results are possibly of a more general nature. Orville [1990] showed that for winter lightning activity there is a close correlation between the maximum lightning intensity and sea surface temperatures. The strong lightning activity at the U.S. east coast might therefore also explain the large number of NOₓ plumes off the U.S. east coast which were observed in autumn and winter of 1995-96 [Brunner et al., 1998] and during the POLINAT 2 campaign in autumn 1997 [Jeker et al., 1998].
7.3 Marine convection and lightning

In remote areas such as the northeastern Atlantic, the base of a convective cloud is often in relatively clean air [Schiff et al. 1979; Helas and Warneck, 1981] due to the rapid decay of short lived pollutants (such as NO\textsubscript{x}) in the boundary layer during their transport across the Atlantic. Here we present such a case of marine convection using several satellite observations to demonstrate that high NO concentrations downwind of convective systems are attributable to lightning. Arnold et al. [1997] provided evidence that strong SO\textsubscript{2} and acetone pollution observed in the northeastern Atlantic originated at the U.S. east coast. Long-range transport of NO\textsubscript{x} from the U.S. east coast therefore potentially needs to be considered when transport times are rapid. In the present case, however, a cut-off low isolated the observed NO plume for at least three to four days, during which U.S. pollution would have decayed to low levels.

On the flight from Zurich to Atlanta on August 14, 1997 a NO plume extending about 1000 km along the flight track was encountered over the northeastern Atlantic between 7.5\(^\circ\)W/47.5\(^\circ\)N and 25\(^\circ\)W/60\(^\circ\)N (Figure 7.13 and flight track in Figures 7.14 and 7.16). During the 70 minutes (1100-1210 UTC) of plume encounter, three sub-plumes exhibiting peak concentrations in excess of 800 pptv (2 minute average), are separated by local minima of about 400 pptv. The high NO measurements were performed in a cyclone which developed on August 9 southeast of Greenland below a prominent filamentary upper-level PV feature. It reached maturity one day later, remained almost stationary and decayed very slowly during the next 5 days. At 0000 UTC on August 11 the upper-level development led to a cut-off which co-evolved with the surface cyclone as a near-barotropic vortex. Between 0600 UTC on August 13 and 1800 UTC on August 14 convection was triggered on several occasions by the rotating PV-anomaly in regions characterized by high values of relative humidity in the lower troposphere. Such events of deep convection above the Atlantic were observed by the GOES-8 satellite from 0300-1300 UTC 13 August. The brightness-tracing plot in Figure 7.15 shows that the highest clouds reached the altitude of the back trajectories, which were started inside the NO plume.
Figure 7.13. The upper graph shows the aircraft altitude (black line) and the altitude of the tropopause (thin line: PV-2 level, thick line: PV-4 level) along the flight track. The lower graph shows measured ozone (gray line) and the (3 second averaged) NO measurements (black area) from the August 14 flight between Zurich and Chicago.
Figure 7.14. Synoptic situation at 1200 UTC on August 14. The upper PV level development leads to a cut-off formation. The NOXAR flight track is marked with circles and with “X” where the (2 minute averaged) NO concentration exceeded 700 pptv.

Figure 14 shows the shape of the PV cut-off at the flight level (~325K) at 1200 UTC on August 14. The initial flight leg in the troposphere belongs to the high NOx plume, whereas NOx concentrations rapidly decreased and ozone increased when the airplane entered the cut-off of stratospheric air at about 25°W shortly after 1200 UTC. This is consistent with the low-pressure altitude of the ECMWF tropopause; the PV-2 and PV-4 levels extended down to 370 hPa and 350 hPa respectively (Figure 13). The back trajectories starting in the first sub-plume exhibit motion in an almost stationary cut-off low (Figure 7.16, marker A) over the ocean. They oscillated within a band of ±1 PVU around the tropopause (2 PVU) during the previous 60 hours and remained east of 51°W during that period of time. Prior to that, the trajectories descended from the stratosphere where they remained in the range of 2-7 PVU for a period of about 40 hours. The low tropopause therefore most likely prevented any convection from carrying urban pollution to the trajectories.
Figure 7.15. Brightness tracing plot of the trajectories starting on the flight leg between 1115 and 1145 UTC on August 14 where high NO values were observed. Diamonds symbolize the altitude of the trajectories and crosses denote the cloud top temperatures of the respective air masses. It can be derived that about 26 hours prior to start of the trajectories convective clouds (from marine thunderstorms) reached the altitudes of the trajectories.

Figure 7.16. OTD overpass from 0923 and 0936 UTC on August 13, 1997. The NOXAR flight track of August 14 is marked with a gray line. The back trajectories (deep purple) are started in the NO plume and crossed an area where the OTD sensor reported lightning activity (contours at −30°E) during its overpass. The location of the trajectories between 0800 and 1000 UTC are marked with green markers. “A” marks the air motion in a cut-off low, “B” marks trajectories, at the U.S. east coast, which were in the stratosphere (PV > 5PVU).
Selected case studies

Trajectories starting in the two following sub-plumes exhibited similar motions. Based upon brightness temperature tracing plots and animated GOES-8 images, we found no evidence that convection over northern Canada (or over the coast) could have transported significant amounts of anthropogenic NO\textsubscript{x} to cruising altitude (marker B in Figure 7.16).

Although the NO plume was observed in the troposphere, the air masses have a stratospheric history as indicated by the evolution of the trajectories' PV values, and points to the importance of stratosphere-to-troposphere exchange events associated with deep convection [Poulida et al., 1996]. Parts of the NO\textsubscript{x} concentration increase during the plume might therefore be attributed to stratospheric NO\textsubscript{y} sources as it is known that in the lower stratosphere, there may be a strong correlation between O\textsubscript{3} and NO\textsubscript{y} [Murphy et al., 1993]. However, based upon the averaged NO\textsubscript{x} concentration profiles (scaled with respect to the tropopause) which were obtained in the North Atlantic Flight Corridor during NOXAR [Brunner et al., submitted] and POLINAT 2 (Figures 8.2 a and b), we believe that the stratospheric influence on the observed NO plume might only be of the order of 200 pptv when most conservative assumptions are made. A second indication that the stratospheric source is probably of minor importance is the fact that the NO and the ozone concentrations are not correlated. Finally and most importantly, as soon as the aircraft entered the stratosphere (high PV and ozone in Figure 7.13), the NO\textsubscript{x} plume disappeared almost immediately.

Schlager et al. [1997] have reported a series of in-situ measurements inside a stationary anti-cyclone in which they attribute large parts of the observed NO\textsubscript{x} concentration increase to accumulated air-traffic emissions into the North Atlantic Flight corridor. Aircraft emissions therefore need to be considered as a potential source. With the method described in 6.2.2.3 we calculated the contributions of aircraft emissions along individual trajectories starting inside the plume. An analysis of the potential aircraft influence according to the procedure presented in section 3.5 of this work, suggests that emissions may only have accounted for maximally 130 pptv when accumulation (i.e. eternal lifetime) is assumed to have taken place over the previous five days. (Remember that this number needs to be seen as a rough estimate only).

It appears that the sum of the NO concentrations resulting from U.S. continental outflow, from stratosphere-to-troposphere-exchange and from air-traffic is significantly lower than the high NO concentrations observed during the marine plume. It is therefore very likely that these elevated NO levels were produced locally in one or more marine thunderstorms.
This hypothesis is supported by the observations of several satellites. At 0932 UTC the OTD lightning sensor overflew the convective cells, viewing the system for about 190 seconds. During this time, 105 total flashes (sum of cloud-to-ground and intracloud) were observed in at least 6 convective cells, spanning an area of about 50,000 km². A coherent set of trajectories starting inside the NO plume crossed this area with enhanced lightning activity between 28 and 32°W/43.5 to 46°N at about the time when the lightning took place (Figure 7.15). Using 70% to 55% as a preliminary estimate of OTD detection efficiency [Boccioppio et al., in press], we estimate that the six cells had total flash rates of (1-2), (1-2), (2-2), (5-7), (11-15) and (24-30) flashes per minute, respectively. The latter rate indicates a significantly electrified deep convective storm. After 1300 UTC 970813, the cluster weakened considerably. Lightning was not observed during the OTD overpasses at 0400 and 0700 UTC 970814. Examination of the spatial agreement of successive OTD-observed background scenes suggests that the location errors for these flashes were no greater than 100 km, which should not significantly impact the current results. (A more detailed list of lightning observations can be found in Table 7.2).

We conclude that lightning events about one day prior to the observation are the most likely explanation of the NO plume. Nevertheless the observed NO₃ concentrations exhibited two distinct local minima during the plume encounter (Figure 7.13) which we cannot not explain given the spotty availability of lightning data from the orbiting satellites.
### Selected case studies

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<td>08:00</td>
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<td>10:15</td>
<td>OTD observes 15 flashes in up to 5 storms</td>
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<td>00:50</td>
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<td>03:00</td>
<td>Cloud tops begin to deepen rapidly</td>
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<td>09:32</td>
<td>OTD observes 105 CC flashes in up to 6 storms (see also Figure 15)</td>
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<td>07:00</td>
<td>OTD observes no lightning</td>
</tr>
<tr>
<td></td>
<td>08:00</td>
<td>GAI long range nighttime coverage ends</td>
</tr>
<tr>
<td></td>
<td>11:30</td>
<td>Aircraft observation of NO plume</td>
</tr>
</tbody>
</table>

Table 7.2. Evidence of convective/lightning activity over the North Atlantic in the area of interest.

### 7.4 Plumes over Europe

During POLINAT 2 only a fairly limited number of NO$_x$ plumes over Europe were observed. This can be explained as follows: Reliable measurements from the NOXAR system only become available about 45 minutes after take-off of the B-747. For westbound flights departing at about 0800-1100 UTC from Zurich airport, the aircraft has already reached France’s west coast or the U.K. (depending on the location of the jet stream and thus Swissair’s selection of an efficient route). With the predominant air-motion at cruising altitude taking place in West-East direction, only a small portion of day-time measurements was performed downwind of European land masses, where the probability for convection is significantly larger than over the Atlantic. All major large-scale plumes were therefore sampled on eastbound flights arriving in Zurich shortly after local sunrise. At nighttime these elevated NO$_x$ concentrations were in the form of NO$_2$ due to the titration of NO with ambient ozone. Occasional downtimes of the photolytic converter, required for the NO$_2$ measurements, therefore further reduced the data set of NO$_x$ plumes over Europe.
The most prominent plume observed over Europe is presented here: On the eastbound flight from New York, early in the morning of August 25, 1997 a pronounced NO$_2$ enhancement with three identifiable sub-plumes was observed during the passage over France (Figure 7.17). The flight took place before local sunrise so that NO concentrations (not shown) remained below detection limit. Note that the last-sub plume disappeared as soon as the aircraft started descending into Zurich airport (gray shaded area). The elevated NO$_x$ concentrations were therefore constrained to a relatively thin layer below the tropopause. By combining back trajectories with Siemens “BLIDS” lightning detection network, it could be shown that the three sub-plumes all had a history of recent lightning encounters. Lightning impact for the first sub-plume occurred during night-time over the Bay of Biscay, for the second plume about 48 hours over Switzerland and for the third plume a few hours prior to the observation over central France. Since only overview pictures of the lightning situation were available but not digital data, no quantitative estimate of the NO$_x$ concentration versus number of lightning flashes could be made for this case.
Figure 7.17. Upper panel: Strongly elevated NO\textsubscript{2} concentrations (black line with dots) and altitude (gray line) of NOXAR eastbound flight from New York, landing in Zurich at 0500 UTC on August 25, 1997. Lower panel: Lightning activity observed from Siemens Germany’s BLIDS network in period of August 22-24, 1997. Ground-to-cloud flashes are symbolized with (-) and cloud-to-ground flashes with (+). The flight track is symbolized with a black line, with overlaid white line at cruising altitude with ambient pressures smaller than 300 hPa. Back trajectories (thin black lines) start on flight legs with NO\textsubscript{2} concentrations >1.5 ppbv. Small black crosses mark one hour and big crosses 24-hour intervals.
8 Generalization of results

In this chapter, the analysis of the NOx budget is extended and refined. Section 8.1 contains a comparison of NOx concentrations measured during POLINAT 2 and the previous NOXAR measurements. Section 8.2 deals with the source attribution of NOx in the flight corridor, starting with the generalization of the lightning tracing method developed in the last chapter. In 8.2.2 to 8.2.3 also methodological problems of applying the automatic lightning tracing method to a large data set, are discussed. Vertical transport of reactive species such as NOx, by conveyor belts and similar atmospheric features is treated in 8.2.5. Finally, some aspects of representativity of the data set of POLINAT 2 and NOXAR are discussed in 8.3.

8.1 Measured NOx concentrations in autumn 1997

The composite of all tropospheric NOx measurements performed at cruising altitude (defined as the altitude range between 190-300 hPa) between August 13 and November 23, 1997 (Figure 8.1a) shows two marked concentration maxima. In August the plumes were concentrated over the U.S. continent whereas between September and November, they were typically located over the Gulf Stream current. As pointed out in the second case study, it appears that thunderstorms over the Gulf Stream have a major impact on upper tropospheric NOx during that season. The stratospheric measurements (Figure 8.1b) exhibited much lower values, most probably because the large tropospheric NOx plumes only rarely penetrated the tropopause (defined here as 2 PVU). However, on a few occasions, large concentrations enhancements of up to 700 pptv could be observed in the stratosphere. It is not sure whether this is due to cross-tropopause injection of pollutants via convection or whether the ECMWF model did not properly resolve the tropopause altitude in these rare cases. Another, although less likely explanation for the large stratospheric concentrations might be that stratospheric flashes above the thunderstorms [Boeck et al., 1995] caused NOx production.
Generalizations of results

Figure 8.1. Composite of all 2 minute averaged NO\textsubscript{x}\textsuperscript{2} measurements performed at cruising altitude (300-190 hPa) in the period of August 13 to November 23, 1997. (a) The tropospheric concentrations (PV<2PVU) were significantly lower than the (b) stratospheric concentrations (PV>2PVU).

Figure 8.2. (a) Vertical NO\textsubscript{x}\textsuperscript{2} (=NO+NO\textsubscript{2,p}) profile, in the NAFC (top graph) and at the US East Coast.
Figure 8.2 (b) The mean values are connected with a vertical line, the median values are marked with squares. In the plots, the scatter is described by the difference between the 10 and the 90% quantiles and is symbolized with a horizontal line connecting them. The number of 2-minute averages available in each class is indicated at the right hand side of the plot. (Only data between 190-300 hPa have been considered).

Comparison with results from Brunner et al. [1998] show that in the years 1995 and 1997, the mean NO\textsubscript{x}\textsuperscript{*} concentrations at cruising altitude (190-300 hPa) between September and November were very similar and ranged from 100 to 150 pptv over the North Atlantic [40-60°N and 10-40°W] and between 190 and 280 pptv above the U.S. continent [30-60°N and 60-90°W]. (An overview with all horizontal and vertical NO\textsubscript{x}\textsuperscript{*} and O\textsubscript{3} profiles can be found in Jeker et al. [1998]). The vertical NO\textsubscript{x}\textsuperscript{*} profile over the U.S. continent (and the corresponding coast) (Figure 8.2b) shows a distinct maximum of 300 pptv below the tropopause with a considerably lower median value. NO\textsubscript{x} profiles from the North Atlantic are markedly different (Figure 8.2a). This difference can most probably be explained by the lower frequency and intensity of convective events and its accompanying lightning activity over the North Atlantic, as it is suggested from an OTD lightning climatology [Christian and Latham, 1998].

In mid-latitudes the tropopause acts as a barrier for vertical transport of pollutants and lightning-produced NO\textsubscript{x} into the stratosphere so that the resulting plumes spread out and cover large areas even though single convective events are of much smaller size. This observation is in agreement with simulated vertical profiles of lightning-produced NO\textsubscript{x} [Pickering et al., 1998].

The comparatively high NO\textsubscript{x} average value at +25 K in the (pseudo) vertical NAFC profile was further investigated because it could be observed both during autumn of 1995 and during POLINAT 2. This local maximum could be attributed to frequent
crossing of sharp NOx spikes, which can typically be attributed to fresh aircraft exhausts. However, it remains an open question why this particular layer was affected by the crossing of more spikes than the other levels.

8.2 Source attribution of NOx in broad plumes

8.2.1 Fast and slow vertical transport

In previous chapters the lightning tracing analysis technique was introduced. By applying it to a number of cases it could be shown that the so investigated broad plumes had a history of recent exposure to deep convection in common. In this chapter the impact of deep convection on the upper tropospheric NOx budget will be systematically studied by widening the data set to include all suited POLINAT 2 measurements. (The term “suited measurements” will be defined below.)

However, as has been pointed out in chapter 2.2, deep convection is only one mechanism capable of lifting ground-based emissions to the mid or upper troposphere. Conveyer belts [Carlson, 1980; Browning, 1990; Browning, 1999] are another important mechanism and are closely tied to extratropical cyclones. The cold conveyor belt (CCB) is an airflow ahead of a surface warm front, whereas the warm conveyor belt (WCB) rises ahead of the surface cold front and can be deep enough to transport air from the planetary boundary layer to the upper troposphere.

Big cities as well as a high industry density at the U.S. East Coast account for considerable ground-based fossil fuel combustion. The same coastal areas are also an active center for cyclogenesis with many conveyor belts originating there. Hence, urban pollution could not only be lifted into the North Atlantic flight corridor by deep convection but also by such synoptic scale systems [Stohl, 2000]. One of the aims of this chapter is to deconvolute the effects of the (rapid) convective transport and the (slower) synoptic scale conveyor belt mechanism on the UT NOx budget.

The speed at which vertical transport takes place has important implications for chemistry. In chapter 2 it was shown that NOx lifetime is a strong function of altitude (see Figure 2.1). If vertical transport speeds are slow, significant amounts of NOx will decay at lower levels by conversion to HNO3 (by reacting with OH radicals in R 2.17) before reaching cruising altitude. On the other hand, deep convection above a polluted area lifts NOx into a regime where lower temperature and humidity lead to less active NOx sinks and thus increased lifetime. If this model holds, upward transport of NOx would be achieved more efficiently by deep convection than by the “slower moving” conveyor belts.

By adopting a statistical perspective, this chapter considers all broad plumes of POLINAT 2 and so complements the mechanism-based case study approach used in the previous chapters. Simultaneously the benefits and limitations of the underlying light-
ning detection network (NLDN) and of the tracing method will be discussed with cases exemplarily selected from the entire data set. Note that the NLDN covers the U.S. mainland as well as the adjoining coastal areas, which restricts the analysis to measurements performed there.

In the second part of the chapter, the discussion of the impact of deep convection will be widened to include all other routes covered by the B-747 (such as the Asian passage) by making use of the polar orbiting OTD instrument, which provides lightning data on a global scale.

In the third and last part of the chapter air masses slowly ascending from the boundary layer will be investigated as a possible explanation for causing broad plumes.

8.2.2 Automatic NLDN tracing for the entire POLINAT 2 data set

In this sub-section a lightning tracing analysis is being performed for the entire POLINAT 2 data set. It will be tested whether the results of the case studies from the previous chapters are of a general nature.

One way of doing this consists of contrasting the lightning tracing results of the broad-plume data sub-set with flight legs where low NO\textsubscript{x} concentrations were measured (hereafter termed “non plumes”). To allow for a clear separation between these data sub-sets the following definitions (definition 1) were adopted: Broad plumes were visually identified and marked if their mean concentration was larger than 600 pptv (more than double the average background concentration in the NAFC) over a distance of at least 300 km or 20 minutes flight time. Note that broad plumes often exhibit several sub-plumes, which are typically separated by big concentration gradients (see for instance Figures 7.4 and 7.11). From within the identified plumes, only measurements where the 2-minute averaged concentrations exceeded 1000 pptv were considered in the analysis. “Non-plume” air masses on the other hand were defined as follows: A data point must not be part of an aforementioned broad-plume and the 2-minute averaged NO\textsubscript{x} concentration must be less or equal to 150 pptv. It is evident that the threshold values for defining broad plumes as well as “non plumes” could be chosen differently. However, while being well suited for contrasting both ends of the measured concentration range, all measurements lying in the range between 150 and 1000 pptv are ignored using definition 1. However, the results presented below proved to be insensitive to variations of the threshold values within reasonable bounds. Moreover, it will be shown that inclusion of all values between 150 and 1000 pptv does not affect the interpretation of the analysis.

The automatic lightning tracing requires some precautions regarding the use of the lightning data (as opposed to the case-study approach, in which typically ideal situations are presented). Gridded NLDN data was obtained from NASA Marshall for the
entire measurement period. Even though the lightning network seemingly covered all NOXAR measurements, there were occasional downtimes of some lightning sensors or of the NLDN central data processing unit. Unfortunately, the gridded lightning data set at NASA Marshall does not distinguish between "no flash present" and "system not available/NaN" (in a grid cell). No operation protocol could be obtained, which would have permitted to exclude unreliable data from the analysis. Even though downtimes of the NLDN are typically rather short relative to the time period of the running system, this type of error needs to be kept in mind at interpretation time. However, a more frequent but less severe problem is the following:

The history of recent lightning exposures must be reconstructed as utterly as possible. When a trajectory leaves the NLDN's detection domain, flashes can remain undetected so that uncertainty of the accumulated number of lightning flashes increases with every time-step a trajectory spends outside of the detection domain. Trajectories were therefore checked for being contained within the network's boundaries and tagged accordingly, allowing prescribing the uncertainty level at analysis time. Whether an air-parcel is fully contained within the network's detection domain also depends on the size of the scanned area around a trajectory, making it necessary to set tags for each chosen area size.

Owing to the large geographic area covered by the B-747, back trajectories started along NOXAR flight tracks spend only a rather limited time within the U.S. NLDN's detection domain. Naturally, this restricts the overall number of suitable NOXAR measurements for investigating the impact of deep convection on the UT NO\(_x\) budget. As an example, of all POLINAT 2 NO\(_x\) measurements only about 10% fall within the broad-plume or non-plume category while being fully covered by NLDN observations during the two-day period prior to the NO\(_x\) measurement. The effect of the limited geographical scope of the lightning data on the overall data set suitable for an analysis was further investigated. A graphical representation of the number of suitable measurements versus the (permitted) maximum number of steps outside the NLDN's detection domain is given in Figure 8.3.
Most broad plume measurements were performed inside or slightly east of the NLDN’s detection domain. By allowing air masses to leave this domain for a few hours, the (relatively small) broad-plume data set can be nearly doubled. The location of non-plume measurements shows a different geographic distribution: Such measurements are evenly distributed throughout the North Atlantic Flight corridor (NAFC). Hence, the size of this data subset surges continuously as we move further east off the NLDN’s boundaries. For the analysis presented below, a maximum of 3 steps (i.e. hours) outside of the NLDN’s detection domain were permitted.

Now we are ready to investigate the effect of deep convection on all POLINAT 2 measurements. Analysis results are based upon a 48-hour time history and a scanning radius of 350 km (standard scenario). The result of the analysis with these standard parameter set can be summarized with Figure 8.4. The graph consists of two overlaid histograms; one made of data from the broad-plume (B) and one of the non-plume data sub-set (A). The apparent distinction between both histograms shows that both data-sets stem from different populations, which clearly demonstrates the effect of deep convection on the POLINAT 2 measurements: As to be expected from the case-studies, a large fraction (88% in first class) of all non-plume air masses (light gray) were exposed to small numbers of (accumulated) lightning flashes. The adjoining class amounts for the second biggest share (6%) of non-plume measurements, leaving all other classes only insignificantly populated.

**Figure 8.3** Number of available NOXAR measurements (2 min. averaged) as a function of maximum permittable number of hours spent outside the NLDN observation range. The upper line represents non-plume (<150 pptv) and the lower line broad plume (>1000 pptv) measurements.
Generalizations of results

Figure 8.4. Two overlaid histograms illustrating the effect of exposure to deep convection (taking lightning flashes as a proxy for convection). Broad plumes are represented in the upper layer, (dark gray, "B") and "non-plumes" in the lower layer (light gray, "A"). Flashes were accumulated over a 48-hour period. Both data sub-sets have same bin size but dark gray bars are drawn thinner to allow viewing of the lower level. The diagram contains 99% of all non-plume and 87% of all broad plume measurements.

The broad-plume sub-set behaves markedly different. Mean and median values of the accumulated lightning flashes far exceed those of the non-plume data set. The statistically significant difference (p=0.001) can be explained by a considerably smaller number of measurements falling into the first class (26%). For all subsequent classes, which contain air masses with a higher number of accumulated lightning flashes, the situation is reversed. These classes are significantly higher populated by broad plume air masses than by the non-plume “control group”. Hence, by taking lightning flashes as a proxy for deep convection and for the production of lightning NOx, this parameter allows rather well to separate air masses belonging to the non-plume and the broad plume class respectively.

However, at first glance the rather high population (26%) of the first class (i.e. a small number of accumulated lightning flashes) of the broad-plume data seems to be contradictory to the hypothesis that broad-plumes are mainly caused by deep convection. As will be shown, a population of the first class by broad plume measurements does not violate the deep convection hypothesis. First, as mentioned above, no information on downtimes of the NLDN was available at analysis time. Coincidence of significant lightning activity and downtimes of the NLDN is possible, which would have underestimated the number of lightning flashes an air mass was exposed to. Second, as mentioned in chapter 6.1.3 the NLDN only detects cloud-to-ground lightning activity. Thunderstorms with high CC-CG ratios are therefore not accounted for appropriately.
leading to an underestimate of the accumulated number of lightning flashes an air mass was exposed to. Third, and probably most importantly: A visual inspection of all broad-plume measurements falling into this first class revealed that most of them were isolated, sharp NO\textsubscript{x} spikes, probably caused by the crossing of young aircraft exhausts. Thus we can conclude that a small number of accumulated lightning flashes does not need to be a contradiction to the deep convection hypothesis, although it can not be proven with the present data sets.

An important aspect to look at is the sensitivity of the result to the selection of the parameter values. In the sensitivity analysis, the standard scenario serves as a base and values of one parameter at a time were changed. Below the sensitivities of the result to a modification of the number of steps outside of the NLDN, the scanning radius and the time to go back are treated one after another.

Interestingly, the number of permitted steps outside the NLDN’s detection domain did not have an impact on the result in any way as long as “reasonable” values between 0 and 10 steps were chosen. Different from that, was there more of a sensitivity to the selection of the scanning radius. It is evident, that the absolute number of accumulated lightning flashes depends on the scanning radius, with bigger radii allowing viewing more thunderstorms and thus a bigger number of flashes. (To account for this problem, one could divide the number of accumulated lightning flashes by the scanning area and thus end up with an accumulated or with an \textit{averaged flash density}. However, such a quantity only makes sense in areas with a more or less uniform distribution of lightning flashes. Lightning fields show sharp gradients and are therefore far from homogeneous. Thus, for our analysis this concept was not adopted.)

As to be expected, bigger scanning radii were accompanied by larger number of lightning flashes, which stretched the histogram in the direction of the x-axis. Both the non-plume and the broad-plume data set were equally affected, thus leaving the significant difference between the two data sets unaffected. However, an important deviation from the standard case could only be observed at smaller scanning radii. There, the broad-plume data set started to populate classes with very few lightning flashes, thus weakening the contrast to the non-plume class. But as had already been concluded in the case-study chapter, this is most probably a sign that the scanning radius had gotten too small in relation to the deviations between real and model air-parcel as a consequence of trajectory errors.

The only instability of the result is related to changes of the length of the time history that is considered in the analysis. In our case the strong contrast of the accumulated number of lightning flashes between non-plume and broad-plumes slowly fades away when air masses are traced back for more than 60 hours. This is not a new observation. Recall that to obtain NO\textsubscript{x}-lightning correlations in chapter 7.1, an exponential decay...
Generalizations of results

factor was introduced, which gives older lightning flashes less weight. It was argued that the three main reasons for such a factor were chemical decay, atmospheric dilution and location uncertainty (of air masses) associated with trajectory errors. Recall also that the concept of “most recent convection” was adopted in the case studies, by which only the most recent convective events were considered in the analysis. In summary, by considering a time history of 48 hours, a big contrast between the number of accumulated lightning flashes of broad-plume and non-plume air masses can be seen. However, the more the time history is extended, the more this contrast fades away. Although some tentative reasons are given above, further research in this field is required.

The analysis underlying Figure 8.4 only contains air masses, which are located at both extreme ends of the measurement range (<150 pptv and >1000 pptv, respectively). Below it will be shown that such a stringent data selection is not necessary to support the convection hypothesis. For this reason, the entire data set is split into two groups of measurements: With it, the first category, the broad plumes must be contained within the above defined, visually identified, air mass and have a concentration in excess of 700 pptv. Non-plumes must not be contained in a visually identified broad plume and have a concentration less than 700 pptv (definition 2). This threshold value was chosen to produce two data sub-sets with a reasonable size for a statistical comparison. By requiring air masses to be fully contained within the NLDN’s domain for 48 hours, 107 broad-plume and 361 non-plume measurements (2-min. averaged) are available for comparison. The result of the analysis are presented in Figure 8.5 a and b. Interestingly, the histograms of both data sub-sets do not differ in any significant manner from those given in Figure 8.4. Note, that by adopting definition 2, the number of non-plume measurements falling into the first lightning class (few lightning flashes) is somewhat smaller than that in Figure 8.4. This behavior is to be expected, because definition 1 excludes all measurements from the “transient zone” between non-plumes and broad-plumes. Nevertheless, the probability of populating any other class is always higher for the non-plume air masses than for the plume air masses. Although less sharp, this latter analysis further strengthens evidence for the convection hypothesis.

Note, that by having larger data sets than with definition 1, another question can be answered as well: “What is the probability of encountering a broad-plume sample, for a given number of accumulated lightning flashes the air mass experienced during the previous 48 hours?”

The result of this analysis is given in Figure 8.5c. At small numbers of accumulated lightning flashes, the probability is equally small and generally speaking, it increases with larger numbers of lightning flashes. However, a probability of 1 is only reached for

This only holds for classes containing at least 3 measurements.
one class. A number of factors help to explain this seeming inconsistency with the convection hypothesis. First, as pointed out previously, the separation criteria used to separate between the broad-plume and non-plume data sets are somewhat arbitrary. This results in assigning a number of “transient” measurements (whose histories may not differ significantly) to one or the other category. Second, the fixed area with which we scan along the trajectories might not be appropriate for every thunderstorm type. For very large thunderstorms with large anvils, the scanning area might not be large enough, which leaves lightning flashes undetected. On the other hand, some non-plume air masses might have had lightning flashes assigned without good, owing to too large a scanning area. Both scenarios would result in encounter-probabilities below 1. The length of the considered time history is another uncertainty factor with an analogous argumentation. Similar is the argumentation with spatial shifts in the ECMWF model, which result in trajectory errors (see also 7.2 and 8.2.3). Third, the mentioned uncertainties with downtimes of the system might explain too small lightning numbers for some (broad-plume) air masses. Fourth, it is possible that air masses were exposed to lightning produced NO\textsubscript{x} or ground-based emissions, which were not lifted to the B-747’s flight track. It can be concluded that not all air masses, which were (seemingly) exposed to deep convection during the previous 48 hours, were broad-plume measurements. A few tentative suggestions are given, which may explain the resulting contradiction to the lightning hypothesis.

Despite all these uncertainties, the results presented in Figures 8.4 and Figure 8.5 strongly suggest that deep convection was in fact the dominant factor for causing broad plumes during POLINAT 2. One more investigation is necessary to further strengthen the case for the convection hypothesis. It will have to be tested whether the occurrence of deep convection was not collinear with that of conveyor belts, which in the positive case, could be the explanation for the high NO\textsubscript{x} concentrations. In this analysis the ascent characteristics of all broad plume air masses were investigated. In a first step it was checked what fraction of all (manually) marked broad-plume air masses ascended from levels below 800 hPa. The result is presented in table 8.1.
Generalizations of results

Figure 8.5. Upper two panels, same as Figure 8.4 but in two different. (a) Top panel: non-plume air masses. (b) Middle panel: plume air masses. (c) Bottom panel: probability of plume encounter.

On average only about 8% (median 2%) of the air masses within a broad plume ascended from such low levels, making it unlikely that conveyor belts were a major factor in causing the broad NO$_x$ plumes during POLINAT 2. Moreover, it is rather astonishing that these slowly ascending air masses, even though embedded in large-scale plumes, typically contained rather small NO$_x$ concentrations (mean=253 pptv, median=173 pptv).

Ascent in conveyor belts is therefore not an explanation for the high NO$_x$ concentrations observed in broad-plumes. The only exception, in which higher concentrations (mean=786 pptv) coincided with ascent from low levels, could be traced back to a number of mesoscale thunderstorms (with anvils having diameters of several thousand km) taking place on August 24, 1997 - stretching from the states of Texas to Louisiana. Closer investigation revealed that all these air masses were also exposed to a significant number of lightning discharges. By excluding this case from the analysis, it can be concluded that ascending air masses are not the explanation for the observed broad plumes.
Table 8.1. Overview of all broad plumes encountered during POLINAT 2 and embedded air masses exhibiting synoptic-scale ascent from below 800 hPa during the previous five days.

By summarizing all results from this chapter, it can be concluded that broad NOx plumes encountered at the U.S. east coast (during POLINAT 2) can typically be attributed to processes associated with deep convection such as rapid upward transport of pollutants from the boundary layer and/or NOx production from lightning discharges. However, elevated numbers of accumulated lightning flashes are not a sufficient criterion for encountering broad-plumes (in every case). A number of shortcomings of the lightning tracing method were presented which might explain this seeming contradiction to the convection hypothesis.
8.2.3 More NO$_x$-lightning correlations and Outlook

The preceding section showed that during POLINAT 2, broad plumes typically had a history with a significantly higher number of accumulated lightning flashes than non-plume air masses. NO$_x$-lightning correlations identified in chapter 7 well prepared the ground for such a hypothesis. In this section the case is strengthened with the presentation of a few more correlations. However, it will be shown that a number of factors need to be fulfilled in order to find such correlations. This will be demonstrated on three exemplary cases. Last but not least the section also serves as an outlook and contains suggestions for further research. The following conditions need to be fulfilled to find NO$_x$-lightning correlations:

1. The exposure of an air masses to recent lightning exposures must be well reconstructable
2. Plumes must have a large enough horizontal extension
3. The concentration enhancements within a broad-plume should exhibit significant variability

The first point was already required in the previous section. However, in the light of a quantitative analysis, it gains further importance: Trajectories often leave the NLDN’s detection domain, during which lightning episodes remain concealed. Affected measurements therefore need to be excluded from the analysis, to avoid underestimating the numbers of accumulated lightning flashes. The second point can be justified as follows: ECMWF fields are at the heart of the lightning tracing analysis. It is important that the horizontal size of the smallest investigated broad-plumes matches at least the model’s resolution. However, the so derived value of about 100 km is likely to be too small: Note, that spatial shifts (see Figure 8.8) over the distance of a few cells are a common problem in the output of numerical weather prediction models, so that it is safe to multiply the aforementioned value with a safety factor.

At first glance, the third point appears to be marginal when looking at individual broad-plumes. Ideally, in the NO$_x$-lightning analysis, data from several broad-plumes could be mixed and all used for establishing a “generally valid” NO$_x$-lightning correlation. However, this task is complicated by a number of uncertainties, inherently present in the NLDN data. Most importantly, as pointed out in section 6.1.3, varies the CG-IG ratio by two orders of magnitude across the U.S. Since only CG flashes are detected with the ground-based network, more or less severe deviations from the relevant number of (CG+IC) lightning flashes (which affects the NO$_x$ content of the air mass) are expected for thunderstorms taking place mainly in one or the other sub-region of the NLDN’s domain. Therefore, it is believed that correlations should be sought on a case-
per-case basis and data from different cases (between which slopes may vary considerably) should not be mixed.

Before a few more NO$_x$-lightning correlations are presented, three exemplary cases, in which no reasonable correlations could be obtained, are presented below. The first (Figure 8.6) and the second case (Figure 8.7) deal with the mentioned geographic variations of the IC:CG lightning ratio. The region of convective influence for a very large NO$_2$ plume encountered over the North Atlantic on November 7, 1997 ranged from the U.S. states of Arkansas to Mississippi (Figure 8.6). According to Figure 6.2, the IC:CG ratio varies from 3.5 (Arkansas) to 2 (Mississippi) and could therefore explain the observed differences in the curve shapes between the time-series of the number of accumulated lightning flashes and the measured NO$_x$ concentrations. Note, however, that the locations of strong gradients in both time-series correspond rather well.

![Figure 8.6](image)

Figure: 8.6. Left panel: Upper graph shows the shape of very large NO$_2$ plume encountered over the North Atlantic on November 7. The lower graph shows the corresponding number of accumulated lightning flashes. The left panel shows the trajectories' paths (dots) and influence regions of convective influence (*). A similar case is that encountered on August 15, 1997. Note that convective influence took place over a very big area between Texas and the Great Lakes. The corresponding IC:CG ratios can achieve values up to four in Texas and are typically around one near the Great Lakes. As in the previous case, the shape of the measured NO concentrations and that of the accumulated number of lightning flashes show a rather similar behavior, but no quantitative relation between the two time series can be established. The lack of the latter can probably be attributed to air masses of the individual sub-plumes being exposed to thunderstorms with different IC:CG ratios.
Generalizations of results

The third example illustrates the problem of spatial shifts. A lightning tracing analysis was performed for the sharp NO\textsubscript{x} plume presented in Brunner et al., [1998]. It can be seen that the method detected a significant exposure of some air masses to lightning. However, while the horizontal dimension of the NO\textsubscript{x} spike resembles that of the accumulated lightning flashes, is there a spatial lag of about 100 km between the two time series. Spatial lags affect a number of cases investigated with the lightning tracing analysis. They can most probably be attributed to the known problem of spatial shifts in meteorological fields or to small errors in the starting times of the trajectories (analyzed ECMWF fields are only available at 6 hour intervals and the starting points of trajectories therefore need to be linearly interpolated in space and time to available fields).

Figure 8.7. Same description as in Figure 8.6 but for the entire westbound flight of August 15, 1997.

Figure 8.8. The upper panel shows the NO\textsubscript{x} concentration measured on the NOXAR westbound flight performed between Zurich on Chicago on August 28, 1995 (time indicated in Julian NOXAR time). The lower panel shows the accumulated number of lightning flashes for a "scanning radius" of 400 km and a 1/e decay factor of 1 day.
These three cases illustrate some shortcomings of the lightning tracing method. Some of them are related to problems in the NLDN data or its suitability in applying it to the examined question. The lightning tracing method could be improved by solving the following tasks:

- More refined statistical methods could eventually help to avoid bad correlations between NO\textsubscript{x} and lightning when spatial lags (possibly from the rough temporal and spatial resolution of the used meteorological fields) exist.
- The lightning tracing method should ideally incorporate a better-suited term for describing diffusion of lightning produced NO\textsubscript{x}. Such a term would allow accounting for sub-scale processes not resolved in the ECMWF model.
- The released energy is likely a better measure for the NO\textsubscript{x} production than the number of accumulated lightning flashes used in this study. However, for the time being, only peak current strength is indicated in the NLDN (and NLDN LR) fields. Without further technical improvement, it might be rather challenging to calculate energy solely from this quantity and additional assumptions about voltage and current evolution would have to be made. Field campaigns investigating this aspect are currently in preparation [Noor Gillian, personal communication, University of Alabama, Huntsville, 1999]. Nevertheless, the fact that correlations were seen in a number of cases despite this uncertainty, suggests that by averaging over large numbers of flashes this point loses importance.

Despite all these uncertainties, NO\textsubscript{x}-lightning correlations could also be found for flights performed during the NOXAR 1995-96 mission. Table 8.2 lists a few additional correlations to that already presented in chapter 7. The table is not exhaustive on this aspect but needs to be seen as a motivation to mine the entire NOXAR 1995-96 data set for correlations, once some of the mentioned uncertainties have been solved.

The observed NO\textsubscript{x}-lightning correlations suggest that plumes consist to a significant extent of lightning produced NO\textsubscript{x} or to processes associated with deep convection (such as the upward transport of pollutants). Note that the slopes in various cases varied within a factor of 6. This value is compatible with all listed error sources but it could be further confined if some of the mentioned challenges are overcome.

Alternatively, as mentioned in section 7.1, the number of accumulated lightning flashes could be interpreted as a proxy for the strength of vertical upward transport. Regression analysis over polluted areas should therefore yield larger NO\textsubscript{x}-flash slopes. However, at the present stage, uncertainties associated with the lightning observations as well as only unsatisfactorily characterized emission inventories prevent us from performing such an analysis. For conclusive evidence on the lightning origin of observed NO\textsubscript{x}
Generalizations of results

plumes, simultaneous measurements of tracers for anthropogenic activity would be required.

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<td>0.84</td>
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Table 8.2. Example of large-scale plumes with NO$_x$-lightning correlations. Bracketed numbers were not determined with linear regression but with the method explained in the text. The Nov. 09 case (section 7.2) was not included due to large uncertainties of the NLDN LR’s detection efficiency.

If the NO$_x$-lightning correlation could be further confined, it could also be used to estimate the NO$_x$ production rate of individual thunderstorms or that of individual flashes. However, many additional assumptions such as the updraft volume would have to be made and thus further increase uncertainty. Modelers, on the other hand would have to go back and introduce similar uncertainties when they distribute produced NO$_x$, which was estimated from NO$_x$-lightning correlations. Hence, at the present stage if the NO$_x$ field is of primary interest to a modeler and the exact partitioning between ground sources and lightning production is not of interest, NO$_x$-lightning correlations could be used to generate synthetic NO$_x$ fields from observed (or parameterized) numbers of lightning flashes.

8.2.4 OTD tracing

For remote areas such as Siberia, where extended NO$_x$ plumes were observed rather frequently, no continuous ground-based lightning detection networks are known to exist. Observations from space (such as for instance from the OTD or the Defense Meteorological satellites) allow performing qualitative lightning tracing, at least for the short time where a trajectory section is viewed by the orbiting platform. Here, results from “OTD-tracing” are presented for plumes measured over remote areas, where satellite measurements are the only lightning observation with good spatial accuracy. (Plumes occurring at the US East Coast were excluded from the analysis because lightning tracing with the ground-based network yields more quantitative results).

Since air masses along a reverse-trajectory are observed only intermittently, it does not make sense to accumulate (instantaneous) OTD-observed lightning flash rates and correlate them to measured NO$_x$ concentrations, as in the lightning tracing method.
“OTD-tracing” therefore only allows pinpointing air masses which were exposed to thunderstorms, but no proof of the opposite can be made because transient thunderstorms could exhibit lightning activity exclusively during the much longer period between two OTD scans.

In the analysis, all manually labeled extended NO plumes of the NOXAR 1995-96 data archive [Brunner, 1998] were considered, for mean plume concentrations exceeding 750 pptv. Tracing was performed as follows:

Three 3-day reverse trajectories were started from the first, middle and last measurement of the NOx plume and coherence of the air-motion classified (c: coherent, s: slightly diverging trajectories, n: non-coherent trajectories). Coherent motion is an important condition for obtaining reliable results. (I.e. in case of non-coherent trajectories it can happen that the trajectories crossed areas with different lightning intensities).

Along each set of trajectories, six bins of 12 hours duration each were filled with observations from OTD intersections. (Fixed geographic areas are viewed about twice a day by the OTD instrument. This assumption also holds for trajectories without rapid longitudinal motion). The following situations are possible:

(a) The trajectory was intercepted by a lightning-exhibiting thunderstorm. The size (and thus type) of the storm system was then categorized into three classes and labeled with “1” if one to three, “2” if four to six and “3” if more than six pixels on the OTD browse image indicated lightning activity. The impact location was recorded and labeled according to the definition given in Figure 8.9.

(b) No lightning activity was detected by the OTD sensor. Such an event is labeled with “•” in table 8.3.

(c) The OTD satellite crossed the area but (at analysis time) no information on lightning activity was available. This category occurs during technical problems of the satellite or when no browse images were available and this class is labeled with “-”.

(d) The trajectory was viewed more than once or not at all during the time interval (see comment above). The first case never occurred and the second possibility only very rarely. The latter was treated like (c).

Results are presented in table 8.3. A simple question to be asked is the following: “What is the probability that a plume has a history with previous lightning encounters?” The probability can be estimated by dividing the number of plumes with lightning encounters (“✓”) by the total number (“x”) of plumes. By excluding all values with no OTD observation in the first 24 hours prior to observation, the following result
Generalizations of results

is obtained: A surprisingly high fraction of 46 out of 62 plumes (74%) had a history of (observed) previous lightning encounters.

If this "manual" investigation holds, then the majority of all investigated NO plumes has a traceable history to a relatively small number of thunderstorms (below 100) most of them belonging to the smallest category. However, the fraction of plumes with an OTD-traceable lightning history seems to vary with season (e.g. October). Another finding is that small (isolated) thunderstorms were much more frequent than the two larger categories.

The number of thunderstorm encounters per geographic area is presented in table 8.4. Probably the most striking result is that a large majority of thunderstorms seems to be traceable to European thunderstorms (note that American thunderstorms were purposely excluded due to the available NLDN data) - possibly an artifact of the aircraft flying to or out of Zurich Kloten airport. This result is very encouraging for further investigations. Combined application of OTD and European networks (e.g. operated by Siemens or the UK Met-Office) should allow quantitative lightning tracing for a relatively large number of plumes. These networks should also be suitable for the Western cells of the high-latitude observations. For the tropical thunderstorms the OTD satellite is probably the only available data source.
**Optical Transient Detector**

*95-05-27*  

**Ascending passes**

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**Figure 8.9.** Quality controlled browse image of the OTD scans performed between 0000-2359 UTC of May 27, 95. Plots are available at the Global Hydrology Resource Center of the NASA Marshall Space Flight Center (http://thunder.msc.nasa.gov/data/otdbrowse.html). The upper panel represents ascending scans (S→N) and the lower panel descending scans (N→S). The viewed area is indicated with blue color over the Ocean and with yellow color over the continents. No measurements are present if the continent appears gray or the ocean white. Red dots indicate lightning flashes. The time where the satellite crossed the equator is indicated in the gray bar at the bottom (UTC) and the top of the graphs (local time). For categorizing impact areas the upper panel was labeled with bold numbers. Satellite status information and cumulated intensity along a scan are indicated at the small panel of the bottom of the graph but not used in the analysis.
## Generalizations of results

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</table>
Table 8.3. Results from OTD tracing performed along back-trajectories started inside marked NO plumes of the 1995-96 NOXAR archive [Brunner, 1998]. Only plumes East of -30E are considered. Plume numbers (#) are given in the first column. The second column (✓) indicates intersection with thunderstorms "✓", no intersection "x". When no OTD availability was present during the first 24 hours a result is questionable and bracketed "( )". Time intervals along the trajectories are labeled with capital letters, "A" representing the time span between measurement and 12 hours prior and "F" the time between 60 and 72 hours prior to the plume observation. In the time interval columns numbers indicate storm size as defined in the text. No lightning activity during the intersection with the trajectory is marked with "•" and with "-" when no OTD measurement was available. Lightning impact areas are indicated with numbers corresponding to Figure 8.9, which are further refined with labels "a" through "d" (The four quadrants are labeled clock-wise starting with "a" in the upper left corner). The last column indicates the coherence of the trajectory: "c" for three coherent trajectories, "s" for "slightly spreading" trajectories and "n" for non-coherent trajectories.

Table 8.4. Convective areas causing broad-plumes on NOXAR flights. For the nomenclature of the cell number refer to Figure 8.9.

Although the presented analysis gives evidence that plumes were often traceable to thunderstorms, a more refined analysis would include a randomly selected control group with trajectories starting on flight sections with low NO concentrations. Another, although less severe problem is the very limited resolution of the browse images and resulting (human) errors during the manual tracing analysis.
Generalizations of results

A joint project has been initiated with the Global Hydrology Resource Center of the NASA Marshall Space Flight Center. OTD tracing has been scheduled for the entire set of NOXAR trajectories. Similarly to the NLDN tracing approach, the “viewing area” around the trajectory as well the temporal tolerance will be varied in an automated algorithm. An interesting way of visualizing obtained results has been proposed by Dennis Boccippio [personal communication, 1999]. For a given NOx concentration: "What is the probability of previous lightning occurrence within T hours of the observation, given OTD within (r,t) km and hours of a reverse trajectory location? (where r and t represent spatial and temporal tolerances employed during tracing)". This result could be contrasted to a plot answering the following question: "What is the probability of no lightning occurrence within T hours of the observation, given OTD within (r,t) km and hours of a reverse trajectory location?"

8.2.5 Impact of slowly ascending air

The role of slowly ascending air masses along fronts was already investigated in section 8.2.2. It was found that such vertical motion was not associated with the high concentrations observed in the broad-plumes. Here the view is widened to include all measurements (plume and non-plume measurements) from the 1995-96 and 1997 missions. Note that slow ascent of air from the lower troposphere has previously been associated with upward transport of pollutants. As will be shown below such reports focused on long-lived species (such as acetone or CO or even CFC's) but no study statistically investigated the situation for the short-lived NOx molecules, for which conditions are expected to be rather different (see also 8.2.1).

Arnold et al. [1997] reported elevated levels of sulfur dioxide, acetone, carbon dioxide and condensation nuclei (CN) from measurements performed over the northeastern Atlantic at 9000 m altitude. The polluted air masses were traced back to the US east coast where ascent from 700 hPa to the sampling altitude occurred in the period of three to five days prior to observation. Other reports stem from Bethan et al. [1998] who highlighted the role of conveyor belts associated with extratropical cyclones for transferring polluted air from the boundary layer to the free troposphere during the development of baroclinic waves. Two warm conveyor belts sampled during a particular flight (one associated with a developing baroclinic wave and the other with a mature low-pressure system) displayed clear and contrasting chemical signatures, a consequence of their geographically different origins. Nevertheless, the number of studies linking such air-streams with chemical tracer measurements remains fairly limited.

Synoptic scale ascent is intrinsically linked to the formation of stratiform rain. Both processes are rather well characterized in numerical weather prediction models (such as ECMWF) due their importance. Output from such a model should therefore yield trust-
worthy results. In the study presented below, trajectories were started for every 2-minute flight-leg performed at cruising altitude (defined by ambient pressures lower than 400 hPa). The analysis revealed that roughly 7% (1253 out of 18301) of all air-parcels (2-minute averaged) sampled in the NAFC and over the US east coast were lifted by synoptic scale ascent from levels below 800 hPa within five days prior to sampling. An overview of all NOXAR flight legs, intersected by such strongly ascending air-streams is presented in Figure 8.10. It can be seen that intersection points between flight tracks and ascending air were distributed relatively evenly throughout the NAFC. For day-time measurements (boxes) intersections were more frequently encountered east of Nova Scotia, with the exception of one flight to Atlanta (which will be separately treated below). Nighttime encounters of ascending air masses (crosses) were somewhat more constrained to western flight legs. Moreover, the graph shows that ascending air-streams often (but not always), intersected extended flight segments and thus affected many consecutive measurements. The (mean) location of ascending trajectories below the 800 hPa level prior to their ascent are depicted in Figure 8.11.
Generalizations of results

Figure 8.10. Intersection points of air-streams ascending from levels below 800 hPa with NOXAR flight tracks during POLINAT 2. Affected (2-min. averaged) nighttime measurements are symbolized with gray crosses. Small squares denote daytime measurements where the measured concentration was smaller than 250 pptv and big squares indicate areas where this limit was exceeded.

Figure 8.11. Mean location of ascending air masses at levels lower than 800 hPa prior to their ascent. Symbols are described in the previous figure. The dashed-dotted rectangle indicates the geographic section of Figure 8.10.
Ascending air thus originated over the Pacific, the US continent, the Gulf of Mexico but predominately over the Carribbeans, the Gulf Stream and in a large cluster located west of the Canary Islands. Regions of enhanced ascent and respective observations are therefore latitudinally separated. It is of relevance for the observed NO\textsubscript{x} concentrations at cruising altitudes to note that during POLINAT 2 no trajectory ascended from the coastal area between the US states of Maine and Maryland where many large cities, industry and power generation facilities produce vast amounts of NO\textsubscript{x}. (This is an artifact of the NOXAR sampling pattern and would probably be different if the B-747 had also served destinations at the US West coast.) These regions from which large scale ascent originates at low altitudes agrees with findings by Wernli and Davies [1997]. They established a one-month climatology of moist air-parcels, which are characterized by a significant depletion of the specific humidity content during ascent. The associated cloud-diabatic heat release was identified to reinforce vertical motions and to lift air parcels to high altitudes. For January 1993, a total of 85 coherent ensembles of trajectories (hereafter referred to as CET) with such characteristic behavior were identified in the north hemisphere. All these rising air masses were then used to estimate the associated mean precipitation rate. The rate agreed with the mean climatological rainfall in the segment of 15N to 60N, indicating that the CETs are indeed responsible for a significant portion of the mid-latitude precipitation. Typical physical processes associated with such CETs were described by Wernli and Davies [1997] and are presented here for one exemplary flight. In Figure 8.12 the flight track from Zurich to Chicago performed on September 7, 1997 is shown. Back trajectories starting on a flight section where NO\textsubscript{x} concentrations exhibited mean and median values of 43 and 46 pptv respectively, emanated from the marine boundary layer of the Gulf Stream region. In line with the CET concept, neighboring trajectories exhibited similar time evolutions of key physical quantities as presented in Figure 8.13.
Figure 8.12. NOXAR flight from Zurich to Chicago performed on September 7, 1997. The bold line symbolizes the flight track and thin lines mark the path of 4-day reverse trajectories emanating from the marine boundary layer.

Figure 8.13a shows temperature along the trajectories and cloud top heights. In the period of 60 to 80 hours prior to the measurement trajectories crossed the warm Gulf Stream current as indicated by the high temperatures of the trajectory and some of the cloud tops. The region is characterized by high reaching convective clouds as indicated by the large scatter of cloud top temperatures with minima as low as −60 deg. C. The CET depicted in Figure 8.12 started to ascend about 60 hours prior to observation. It is in this phase that mean properties of the CET exhibit significant changes. Figure 8.13b shows that latent heat release led to an increase in the potential temperatures by almost 40 deg. C. The time trace of PV in Figure 8.13c illustrates the generation of a diabatically induced positive PV anomaly. Potential vorticity of the air parcels first increased from values typical for lower tropospheric air (0.3-0.5 PVU) to values near 1 PVU below the level of maximum diabatic activity. Thereafter the values decreased to below the initial reference value. In Figure 8.13a it can be seen that the cloud cover above the stream of ascending air broke off at about 10 hours prior to observation, probably because on-going precipitation had sufficiently dried respective air-parcels. A lightning tracing analysis suggested that even though convective clouds were accompanying the flow above the warm Gulf Stream, no flashes were present at any instance.
Figure 8.13. Sub-figures (a) are to (c) are placed from top to bottom. (a) Trajectories (black lines) and cloud top heights (gray stars). (b) Shows the time trace of potential temperature and (c) time the PV evolution.
Generalizations of results

Wernli and Davies [1997] suggested that moist ascending CETs are frequent features of the northern hemispheric wintertime circulation. These processes are linked to, and occur predominantly in the vicinity of the dominant mid-latitude storm tracks of the northern hemisphere. Due to the importance and frequency of these features it is therefore interesting to investigate typical NOx concentrations sampled within such atmospheric features. Results are presented in Figure 8.14.

![Graphs showing NO concentration distributions](image)

**Figure 8.14.** Left graph: Normalized histogram and lognormal fit of all (bold) 2-minute averaged daytime NO observations performed between September and November 1997 in the NAFC. Thin histogram and lognormal fit indicate the sub-set of (n=672) measurements of air masses ascending from levels below 800 hPa. Right graph: Same principle but for sub-set of samples performed over US (bold) and ascending from (thin) the boundary layer of the US continent.

It can be seen that sampling within air masses which previously ascended from low altitudes generally resulted in lower (day-time) NO mixing ratios than sampling performed in the same area but without a history of previous slow ascent. This visual impression was confirmed by a single sided Wilcoxon test which clearly rejected the zero-hypothesis (of the two samples having same mean values) on the p=0.00 and p=0.01 confidence levels, for measurements performed in the NAFC and over the US east coast and continent, respectively. Similar observations were made by SONEX. A particularly good example is the October 20 Azores flight for which the “most probable” NOx mixing ratio was 100 pptv - which is clearly less than more typical values of 200-500 pptv, measured on other mission days. On this Azores flight most probable ozone was about 30 ppbv, which is indicative of ascending air from the marine boundary layer [Thompson et al., 1999].

Statistics performed with nighttime NO2 measurements (not shown), which typically took place in the jet stream, confirmed the picture. However, since these measurements were plagued with larger instrumental noise and off-set problems (see section 4.4.2.2), mixing ratios of ascending air often dropped below the detection limit as opposed to
samples of non-ascending air. These low NO\textsubscript{x} observations can most probably be explained by a combination of factors:

As can be seen in Figure 8.11 most ascending air masses originated in the marine boundary layer 1-5 days prior to observations. At these low altitudes the NO\textsubscript{x} lifetime is of the order of about 0.5 days [Jaeglé et al., 1998] so that pollution plumes vented out from the US mainland rapidly decay. Apart from ships [e.g. Massin and Herz, 1993; Wang et al., 1996], there are no other known sources, which would “recharge” such air with significant amounts of NO\textsubscript{x}. Additionally, in contrast to rapid convective motion, the comparatively slow ascent in CETs gives time for the formation of HNO\textsubscript{3} which easily dissolves in cloud droplets and subsequently scavenged during precipitation, which typically accompanies such vertical motion. The present section thus highlighted that ascending motion of air typically resulted in low NO\textsubscript{x} mixing ratios.

A few comments on the representativity of aforementioned low NO\textsubscript{x} air masses seem appropriate. First, Wernli and Davies [1997] reported various types of CET associated with extra-tropical cyclones. Not all of them reached the B-747’s cruising altitude and so the probability of encountering low “NO\textsubscript{x} pockets” might be higher at lower altitudes. Second, as already mentioned, the pre-defined flight air-route to Atlanta lowers the probability of sampling CETs originating over strong pollution spots between the US states of Maine and Virginia. However, as was shown in Figure 8.14, are NO mixing ratios from such ascent regions also considerably smaller than typical concentrations sampled over the continent (and US east coast).

The situation might be different for other seasons and the data of the 1995-96 NOXAR campaign was therefore mined for ascending CETs. Departure origins of ascending trajectories are presented in Figure 8.15 and a comparison of (day-time) NO concentrations between ascending and non-ascending air masses is given in the histograms in Figure 8.16. The Atlantic seems to be a region of enhanced large-scale ascent throughout the year. However, on the tropical route between Bombay and Hong-Kong the influence of the monsoon is visible for the summer months and particularly pronounced in autumn. Pacific air ascended most frequently during winter, probably due to the comparatively large heat reservoir of the sea relative to the continents. Air from North Africa ascended during the months of March to May 1996. Similar to the findings by Wernli and Davies [1997] ascending air exhibited a pole ward motion and flight tracks were therefore most often north of the source origins. Therefore southernmost air was sampled on the tropical Bombay to Hong-Kong route during monsoon between September and November.

An analysis of (day) NO concentrations from ascending and non-ascending air masses (Figure 8.16) yields similar results to those during POLINAT 2. Air masses starting ascent over different geographic regions such as the Atlantic, Africa, Asia etc. exhibited
Generalizations of results

similar (day-time) NO probability density functions (hereafter referred to as PDF). Therefore only PDFs of the North Atlantic (left side in Figure 8.16) and the US continent (right side) are presented. Conclusions drawn from these regions are equally applicable to other landmasses and oceanic areas.

It is interesting to note that the PDFs of ascending air masses did not exhibit a significant seasonal cycle and that median values always remained below 100 pptv regardless of whether ascent started over the continent or the ocean. However, the sum of all measurements performed at cruising altitude (with and without recent ascent) was subject to a seasonal cycle, most probably due to varying intensities of the convective- and lightning sources. During winter months- when these sources were statistically significantly smaller over the continents and somewhat reduced over the ocean- the difference of the NO mean value between ascending and non-ascending air masses became insignificant as indicated by the large p-values of 0.2 and 0.39 respectively. For the period of March to May 1996 the lognormal fit for ascending air masses is not very appropriate. Reasons are both a comparatively small sample size and a relatively large number of active thunderstorms over the Gulf Stream, which episodically enhance NO concentrations of ascending CETs.

The impact of air masses starting ascent in the strongly polluted New-York Boston area was investigated and is presented in table 8.5. Interestingly mean concentrations for all seasons remained below 120 pptv, implying that polluted air was trapped in the inversion layer- or more likely- that originally high NOx pollution decayed on the way up to cruising altitude due strong activity of the nitric-acid exit path at low altitudes.

<table>
<thead>
<tr>
<th>Season</th>
<th>Number of ascend. trajs.</th>
<th>Mean NO [pptv]</th>
<th>Median NO [pptv]</th>
</tr>
</thead>
<tbody>
<tr>
<td>JJA 95</td>
<td>4</td>
<td>072.5</td>
<td>089.0</td>
</tr>
<tr>
<td>SON 95</td>
<td>10</td>
<td>057.1</td>
<td>050.0</td>
</tr>
<tr>
<td>D 95, JF 96</td>
<td>3</td>
<td>112.0</td>
<td>117.0</td>
</tr>
<tr>
<td>MAM 96</td>
<td>2</td>
<td>031.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table 8.5. NO concentrations contained in air-parcels ascending from the highly polluted New-York Boston area (defined as the area between 38N to 42N / 70W to 78W). Note that the sample size is relatively small but that concentrations are very small.

To summarize, it can be said that slowly ascending air masses generally contained significantly lower NO concentrations than air masses without previous ascent. Part of this difference might be explained by a shorter exposure to aircraft exhausts in the case of ascending air masses. Such air masses were also less frequently exposed to convective motion, which rapidly transports ground pollution and lightning NO to cruising altitude, and therefore largely precludes chemical decay on the way up. Ascending air
from the strongly polluted area between New York and Boston generally contained very low NO\textsubscript{x} concentrations, probably due to efficient wet removal via HNO\textsubscript{3} formation. However, it must be noted that due to the specific flight path to Atlanta, only a very limited number of all trajectories originated from this area.

**Figure 8.15.** Flight tracks and departure points (dots) of air masses ascending from levels below 800 hPa to cruising altitude (defined as pressures equal or smaller than 400 hPa). Letters on the left-hand side of each plot indicate months. Graphs from top to bottom are for June-August 1995 (JJA), September-November 1995 (SON), December 1995-February 1996 (DJF) and March-May 1996 (MAM). Note the seasonal variation of departing origins of ascending trajectories.
Figure 8.16. Left side shows histograms and lognormal fits of (day-time) NO mixing ratios of ascending air masses (thin lines) with marine departure origins. Thick lines indicate histograms and lognormal fits of all measurements (with and without history of previous ascent). Right hand side: Same for US continent.
8.3 Representativity of NOXAR and other aspects

As had been shown in section 5.2 the majority of all NOXAR measurements took place in a close band between ±10 degrees above and below the tropopause. It had been shown several times in the thesis that NOx downwind of thunderstorms is deposited below the tropopause due to the "stratospheric barrier". Since the B-747 operates in midlatitudes with a probability of about 50 % in the uppermost troposphere, the frequency of encountering highly elevated NOx concentrations might therefore be biased by the sampling strategy imposed by flight paths of commercial airliners. This picture is confirmed by Figure 8.17 where light areas indicate higher probability of encountering elevated NOx concentrations. However, vertical profile information (which should now be more reliable due to the frequent calibrations) can be used for constructing a data set, which is also representative for lower altitudes. As could be seen in the European case (and other cases, not presented here), NOx concentrations significantly decreased during final descent into Zurich Kloten airport. Representativity of measured vertical profiles, however, might be limited in situations where approaching aircraft are put in a holding pattern, circling over the destination airport. In this case aircraft exhausts might account for considerable NOx concentration enhancements.

Figure 8.17 also highlights that only a small fraction of high NOx concentrations was observed in the lowermost stratosphere. This finding will be more closely investigated below. Figure 8.18 contains histograms with maxima and minima of all PV values along 5-day back trajectories started inside the same plume air masses as in figure 8.17.

Figure 8.17. Position of plumes relative to tropopause. The tropopause is defined as PV 4 and is indicated by the horizontal line. All marked daytime NO plumes observed during NOXAR 1995-96 were filled into a 5x5 degrees theta grid and a contour of frequency plot made. Numbers indicate the number of plumes contained in each cell. Note that most plumes were confined to a band between the tropopause and ~20K theta below.
Generalizations of results

It can be seen that most plume air masses remained in the troposphere during the previous five days (PV<4PVU). For a limited number of observations, however, air masses were always confined to the stratosphere. Analysis revealed that these cases mainly occurred over Siberia where overshoooting tops of multi-cell thunderstorms possibly penetrated the tropopause. Thus lightning/surface NO$_x$ was deposited into the stratosphere. Such a case occurred on July 25, 1995, over Siberia and strong lightning activity in the area of interest was detected during several OTD scans. Such cases should be further investigated to learn more about this type troposphere-to-stratosphere exchange, which may also be important for the stratospheric water vapor budget.

![Figure 8.18](image)

**Figure 8.18.** Normalized histogram of minimum PV (bold line) and maximum PV (thin line) of 5 day reverse trajectories started in all marked NO$_x$ plumes of the NOXAR 1995-96 campaign. A total of 7231 (2-minute averaged) measurements (with valid trajectories) were considered.

Last but not least, representativity of cloud cover was investigated. In Figure 8.19 it can be seen that the Gulf Stream was characterized by a very high probability of convective clouds reaching cruising altitude. Both SONEX and NOXAR sampled frequently elevated NO$_x$ concentrations downwind of thunderstorms from that rather small but important area.

Different types of analysis in this chapter strongly suggest that convection and lightning were indeed the dominant factors for causing the broad NO$_x$ plumes during POLINAT 2. Unfortunately, the lightning tracing analysis could only be performed for a fraction of all measurements, for which lightning data was continuously available.
Further studies making use of the lightning tracing technique, should clearly address this point by including lightning data from other regions. Such measurements are provided by the U.K. met. Service\(^3\), by Siemens\(^4\), Germany (see also section 7.4), the Central Europe Lightning Detection Network (CELDN)\(^5\), the Slovenian Network\(^6\) and many others. A useful information provider, which compiles data from several lightning detection networks, is indicated in the footnote\(^7\). A rather difficult task might be to

\footnotesize

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\(^3\) http://www-imk.physik.uni-kiel.de/~gmueller/pics/Rsfloc.gif

\(^4\) http://212.126.223.22/default.htm


\(^6\) http://observer.eimv.si/FlashClient/Strele.html

\(^7\) http://www.torro.org.uk/sinfo.htm
Generalizations of results

homogenize such data, which stem from different systems, which use various detection techniques.
9 Conclusions

In the present thesis the nitrogen oxides (NO$_x$) budget at the tropopause is investigated. There, the NO$_x$ field is an important factor for determining the in-situ production of ozone, which acts as a strong greenhouse gas. At these altitudes, the NO$_x$ budget is mainly determined by upward transport of pollutants from the planetary boundary layer, lightning produced NO$_x$, aircraft emissions and NO$_x$ formed from the photolysis of stratospheric N$_2$O with subsequent downward transport.

The study is based on NO$_x$ (NO and NO$_2$) and ozone measurements performed with a fully automated instrument (NOXAR) [Brunner, 1998; Dias-Lalcaca, 1998], permanently installed aboard a Swissair B-747 airliner. For this thesis the system was operated during a four-month period (August 15 - November 23, 1997) within the framework of the coordinated POLINAT 2 and NASA SONEX campaigns and provided data from 98 North Atlantic Flight Corridor (NAFC) passages. Laboratory measurements preceding the 1997 system deployment lead to modifications of the original NO$_x$ calibration procedure, with which measurement uncertainties could be well characterized.

A striking feature of the upper tropospheric NO$_x$ field is the occurrence of large-scale NO$_x$ enhancements (broad plumes) up to several parts per billion by volume (ppbv). Extensive trajectory statistics with data from both NOXAR campaigns suggest that slow ascent of polluted planetary boundary layer air in and near fronts was not a source of the broad plumes at cruising altitude. In fact it was shown that NO$_x$ mixing ratios were generally lower than air masses without a history of prior ascent. It is suggested that these low NO$_x$ concentrations are caused by washout processes (via the formation of nitric acid) associated with the cloud systems typically accompanying strongly ascending motion. The altitude range between the capping inversion and a few kilometers below the tropopause (where NO$_x$ from convective storms is deposited) is suggested to be region of clean air. This hypothesis is supported by a number of flights where NO$_x$ plumes immediately disappeared when the B-747 started final descent into an airport (e.g. European lightning case or the SONEX measurements of November 9, where NO$_x$ was only elevated at high altitudes).

The tropopause scaled vertical NO$_x$ profiles during POLINAT 2 do not give evidence for a significant contribution of stratospheric NO$_x$ to the total NO$_x$ abundance in the lower stratosphere.

The most significant part of the thesis is dedicated to the analysis of lightning production of NO$_x$. Specialized diagnostic tools based on trajectories, satellite imagery and lightning are accurate enough to demonstrate the prominent role of combined effects of convection and lightning in three case studies. In one case-study it was illustrated how convective venting of pollutants and lightning introduced very large scatter in the NO$_x$
field which can make it statistically impossible to discern the effect of aircraft exhausts without additional specific aircraft tracer information (note that no such tracer could be found during SONEX).

The usefulness of convective influence maps is confirmed and a new technique called "lightning tracing" showed that for some plumes accumulated flashes along a parcel trajectory were proportional to NO\textsubscript{x} concentrations several hundred km downwind. Indeed, for two consecutive events studied in detail, the flash-NO\textsubscript{x} proportionality was the same. Correlations were also found on other flights both from the first NOXAR campaign and from POLINAT 2. Such flash-NO\textsubscript{x} proportionalities demonstrate the dominance of the convective and lightning sources on the upper tropospheric NO\textsubscript{x} budget in the aftermath of thunderstorms.

For robust NO\textsubscript{x}-lightning correlations to show up in the analysis, a number of factors need to be fulfilled. It is shown that non-compliance with one or more of these factors can conceal the proportionalities. Along those lines, it is suggested that the lack of availability of intracloud lightning data is an important but inevitable uncertainty of the lightning tracing analysis. Because research on the IC:CG ratio and its impact on the lightning production of NO\textsubscript{x} is still in its infancy, this uncertainty may only be overcome with data from future generation geostationary satellites hosting lightning detectors aboard. Erroneous geographical shifts in meteorological models are another challenge to be treated in future extensions of the lightning tracing technique.

A statistical analysis using all POLLNAT 2 measurements clearly demonstrated the predominant role of convection and lightning in causing NO\textsubscript{x} plumes at cruising altitude: Broad plumes encountered at the U.S. east coast typically had a history of recent exposure to lightning flashes, which can be seen as a proxy for both the rapid upward transport of pollutants from the boundary layer and/or NO\textsubscript{x} production from lightning discharges. However, elevated numbers of accumulated lightning flashes are not a sufficient condition for encountering broad plumes at cruising altitude. The aforementioned shortcomings of the lightning tracing method are believed to be causing this seeming inconsistency with the convection hypothesis.

To overcome the limitations of the U.S. NLDN's detection domain, observations from the OTD lightning detection satellite were used to investigate the origin of all major broad plumes from the first campaign. Even though this orbiting satellite views the respective air-parcels (described by the back trajectories) only for a short periods of time, an unexpectedly high number of reverse trajectories starting inside NO\textsubscript{x} plumes intersected active thunderstorms. To strengthen the case, trajectories started on flight sections with low NO concentrations must also be examined. This is planned work in a joint project with the Global Hydrology Resource Center of the NASA MSFC.
It is recognized that lightning potentially coincides with convective injection of surface NO\textsubscript{x} pollution, and that there is not always sufficient data to discriminate between the two processes. Tracers for combustion processes such as carbon monoxide (CO) would help to separate between the two sources. (In this view, the current upgrade of the MOZAIC measurement system with CO detectors is a promising enterprise.\textsuperscript{8})

In two of the three cases that were studied in detail, however, lightning was associated with marine convection and surface sources were minimal, which gives the lightning component more weight. The question for evaluating the North Atlantic Flight Corridor NO\textsubscript{x} budget becomes: how typical was the 1997 period in relation to other years? One of the (late autumn) cases describes large scale NO enhancements downwind of a cluster of marine thunderstorms triggered over the warm waters of the Gulf Stream. Indeed, a composite produced from all available GOES-8 IR images showed that the autumn 1997 period was characterized by high thunderstorm probability above the Gulf Stream. This phenomenon also led to lower-than-usual PV values along the SONEX mission flight tracks [Thompson et al., 1999]. Sampling downwind of the convective clouds triggered in this area generally resulted in very elevated NO\textsubscript{x} concentrations sampled by both the NASA DC-8 and the NOXAR instrument and associated plumes were sometimes vented very far with the jet stream.

The concentration range of our NO\textsubscript{x} plume observations, typically detected a few hundred km downwind of thunderstorms, is similar to those reported for anvil penetrations in the literature [Huntrieser et al., 1999]. They are consistent with a mechanism in which strong mixing in an active storm rapidly reduces and dissipates the initial high, heterogeneous NO\textsubscript{x} field [Stith et al., 1999]. Thus, similar concentrations might be measured from the NOXAR aircraft several hours or several days later as weak mixing downwind preserves a plume (and NO\textsubscript{x}-flash correlations) during transport.

Some comments are made with regard to representativity of the NO\textsubscript{x} field sampled by NOXAR. Due to the inherent sampling pattern around the tropopause, NOXAR may underestimate the importance of clean marine air to the overall atmosphere. On the other hand, largest fractions of (simulated) lightning generated NO\textsubscript{x} were deposited below the tropopause [Pickering et al., 1998; Allen et al., 2000]. This type of NO\textsubscript{x} signature therefore gets a high probability in mid-latitudes.

\textsuperscript{8}http://www.aero.obs-mip.fr/mozaic/
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International Workshops and Conferences
- POLINAT (Pollution in the North Atlantic) workshop, coordination meeting for measuring campaign, June 1997, in Oslo, Norway.
- First NASA SONEX science team meeting, "Overview Swissair B-747 measurements during POLINAT 2/SONEX", oral presentation, June 1998, in Atlanta (GA), USA
- Oral presentations at Atmospheric Effects of Aviation Conference, Virginia Beach, USA, April, 1999 and at The Global Hydrology Resource Center of the NASA MSFC in Huntsville, USA: “NOx signatures from marine lightning - Observations from B-747 measurements".
Curriculum Vitae

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