Doctoral Thesis

Volatile organic compounds and their oxidation products in the atmospheric boundary layer laboratory and field experiments

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VOLATILE ORGANIC COMPOUNDS AND THEIR OXIDATION PRODUCTS IN THE ATMOSPHERIC BOUNDARY LAYER: LABORATORY AND FIELD EXPERIMENTS

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH
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Contents

Summary vii
Zusammenfassung v

1 Introduction 3
1.1 Overview of the thesis .................................. 3
1.2 Background ............................................ 4
  1.2.1 Ozone formation in the planetary boundary layer and the role of VOCs 4
  1.2.2 Ozone formation under the presence of VOCs 5
  1.2.3 Secondary aerosol formation 8
  1.2.4 Long-range transport of air pollutants 9
  1.2.5 Transport within and above mountainous terrain 10
1.3 Proton Transfer Reaction Mass Spectrometry 10
  1.3.1 Calculation of the reaction time t 12
  1.3.2 Calculation of the effective temperature 14
  1.3.3 Calculation of the reaction rate constants 15
  1.3.4 Recommendations for using the PTR-MS 16
1.4 Laboratory and field studies of this thesis 17
References .............................................. 19

2 Performance Characteristics of a Proton Transfer Reaction Mass Spectrometer Derived From Laboratory and Field Measurements 27
2.1 Introduction ........................................ 28
2.2 Experimental ...................................... 29
  2.2.1 PTR-MS methodology 29
  2.2.2 PTR-MS setup 30
  2.2.3 Other VOC analyzers 31
  2.2.4 Measurement locations 31
2.3 Results and discussion 32
  2.3.1 Temperature dependence of the background signal 32
  2.3.2 Mass discrimination 35
2.3.3 Humidity dependence of the benzene sensitivity .......... 37
2.3.4 Formaldehyde comparison .......................... 40
2.3.5 Instrument intercomparison .......................... 43
2.3.6 Measurements of aromatics, PTR-MS comparison with GC . 44
2.4 Conclusions ............................................. 48
Acknowledgements ........................................... 50
References .................................................. 50

3 Reaction Chamber Studies of the 1,3,5-Trimethylbenzene/NOx
Photooxidation ............................................. 57
3.1 Introduction ............................................ 57
3.2 Experimental ........................................... 57
3.2.1 Chamber description and experimental procedure ........ 57
3.2.2 Instrumentation ...................................... 58
3.3 Master Chemical Mechanism ............................. 59
3.4 Chemical reactions leading to radicals ..................... 60
3.5 Results .................................................. 63
3.6 Conclusions and Outlook ................................ 69
References .................................................. 69

4 Volatile organic compounds in the Po Basin. Part A: anthropogenic VOCs ..... 73
4.1 Introduction ............................................. 74
4.2 Measurement sites, techniques, and meteorological conditions . 75
4.2.1 Measurement sites .................................... 75
4.2.2 Trace gas measurements ............................. 76
4.2.3 Meteorological conditions and ozone concentrations .... 77
4.3 Results and Discussion .................................. 78
4.3.1 Aromatic compounds ................................ 78
4.3.2 Cyclohexane ......................................... 84
4.3.3 Receptor modeling using positive matrix factorization analysis 85
4.4 Conclusions ............................................. 90
Acknowledgements ........................................... 91
References .................................................. 91

5 Volatile organic compounds in the Po Basin. Part B: biogenic VOCs .............. 95
5.1 Introduction ............................................. 96
5.2 Sampling site and instruments ............................ 97
5.3 Results and discussion .................................. 98
5.3.1 Isoprene, methyl vinyl ketone, and methacrolein ......... 98
5.3.2 Methanol ............................................. 110
Contents

5.4 Conclusions .................................................. 112
Acknowledgements ........................................... 113
References ...................................................... 113

6 Nocturnal Trans-Alpine Transport of Ozone and its Effects on Air Quality on the Swiss Plateau .......................... 121
6.1 Introduction ................................................ 122
6.2 Measurement sites ........................................ 123
6.3 Results and discussion ..................................... 125
  6.3.1 Ozone and formaldehyde levels during the CHAPOP campaign 125
  6.3.2 Ozone at Cimetta (1672 m asl, south of the Alpine crest) .. 128
  6.3.3 A case study of ozone transport from south to north of the Alps ................................................ 131
  6.3.4 Air flow across the Alps ................................ 132
  6.3.5 Ozone at Rigi (1030 m asl, north of the Alpine crest) .... 133
  6.3.6 Implications for the Swiss Plateau north of the Alps .... 136
6.4 Conclusions ................................................ 137
Acknowledgements ........................................... 138
References ...................................................... 138

7 Final Remarks and Outlook ................................. 143
References ...................................................... 145

Acknowledgements ........................................... 147

List of Publications ......................................... 149

Curriculum vitae ............................................ 151
Summary

Volatile organic compounds (VOCs) play a central role in chemistry of the troposphere e.g. due to the production of ozone in the presence of nitrogen oxides and sunlight. Beside the climatic effect of ozone and some VOCs as direct greenhouse gases, VOCs can influence the climate through their production of organic aerosols. Both anthropogenic and biogenic emissions contribute to the release of these species into the atmosphere.

In this work, instrument characterizations, laboratory studies in a reaction chamber, field campaigns, box model simulations, and statistical analyses of perennial data series were performed to characterize the role of VOCs and their oxidation products in the polluted boundary layer.

Most common methods for measuring VOCs are flask sampling and subsequent off-line analysis in the laboratory or in-situ analysis by gas chromatography (GC). Flask sampling cannot supply continuous data and GC techniques usually need pre-concentration procedures that can cause sampling artifacts and are at the expense of a high time resolution.

A proton transfer reaction mass spectrometry (PTR-MS) was implemented as a novel measurement technique that avoids lengthy sampling and analytical procedures. It emerged as a useful technique for measuring a multitude of VOCs with a high time resolution and a low detection limit. Extensive performance tests in the laboratory and the field revealed the necessity of a detailed characterization including the dependence of the instrumental sensitivity on environmental conditions and the instrumental settings of the instrument. As only the masses of the ion and not specific VOCs are determined, different isomers cannot be resolved and unknown contributors to a certain mass can never be completely excluded. Therefore, the reliability of the PTR-MS results depends for some masses on the atmospheric VOC pattern as shown by means of GC - PTR-MS comparisons. Consequently, parallel measurements with another technique (e.g. gas chromatography) are recommended, especially when measuring aged air masses with anthropogenic and biogenic VOC contributions.

Reaction chamber studies were conducted to investigate the photooxidation and the formation of secondary organic aerosols of a 1,3,5-trimethylbenzene/NO_x system under controlled conditions. The monitoring of the reactants and their oxidation products with PTR-MS showed a to some extent reasonable agreement
with box model simulations. However, the measurements of the organic gas-phase species by PTR-MS and a multitude of inorganic compounds with different instruments contributed significantly to an improved understanding of the SOA formation from gaseous precursors. It was found that the SOA formation is considerably favored by polymerization processes on the surfaces of homogeneously nucleated aerosols.

Two field campaigns were performed in the Po Basin to learn more about the role of different VOCs producing formaldehyde and the role of formaldehyde as an intermediate of the VOC oxidation in the atmospheric boundary layer. An analysis of these VOC measurements together with results from a former campaign and routinely performed measurements from the local Environmental Office enabled the identification of different anthropogenic VOC patterns in August compared to July and September and on weekends compared to weekdays. In August, reduced anthropogenic emissions were observed related to a vacation effect when industrial activities and traffic densities are decreased. Diurnal cycles of isoprene, a VOC mainly of biogenic origin, at a semi-rural site in the Po Basin showed a bimodal diurnal profile not explainable when only the estimated isoprene emissions were considered. The pattern could be reproduced by a three-dimensional Eulerian model and could be explained by the interaction of emissions, vertical mixing, and chemistry. Nighttime processes that are important as they determine the initial conditions for the next day’s photochemistry were analyzed and the reactions of isoprene with NO3 radicals determined to be the most responsible processes for the decay of isoprene after sunset.

Trace gas measurements in the Leventina valley in southern Switzerland were performed to study the vertical mass exchange and the effects of the traffic emissions in several heights above the valley bottom. A recurrent feature with highest concentrations of secondary air pollutants was observed at an elevated site during nights with southerly winds. An analysis of a perennial ozone time series generalized the finding and attributed the enhanced nighttime concentrations to residual layer air from the Po Basin. Such air masses can be transported during the night across the Alps resulting in enhanced ozone concentrations even in the residual layer north of the Alps. As the trace gas levels in the residual layer air supply the initial conditions for the ozone formation of the next day in the atmospheric boundary layer, the nocturnal trans-Alpine transport of ozone can even influence the air quality of the atmospheric boundary layer on the Swiss Plateau as it is shown for the rural station Taenikon, located in the east of the Swiss Plateau.
Zusammenfassung

Flüchtige organische Verbindungen (engl.: volatile organic compounds; VOCs) spielen vor allem aufgrund ihrer Funktion bei der troposphärischen Ozonproduktion eine zentrale Rolle in der Atmosphärenchemie der Troposphäre. Neben dem direkten klimatischen Effekt von Ozon und gewissen VOCs aufgrund ihrer Wirkung als Treibhausgase, können VOCs das Klima der Atmosphäre durch die Bildung von Aerosolen verändern. Sowohl anthropogene als auch biogene Prozesse tragen zur Freisetzung dieser Spezies in die Atmosphäre bei.

Im Rahmen dieser Arbeit wurden Instrumentencharakterisierungen, Laborstudien in einer Reaktionskammer, Feldmessungen, Box-Modell Simulationen und statistische Analysen langjähriger Zeitreihen durchgeführt, um die Rolle der VOCs und ihrer Oxidationsprodukte in der verschmutzten atmosphärischen Grenzschicht zu untersuchen.


Zusammenfassung

Masse wenn gealterte Luftmassen gemessen werden, die von anthropogenen und biogenen Quellen beeinflusst sind.


die Spurengaskonzentrationen in der Reservoirschicht die Startbedingungen der Ozonbildung des nächsten Tages vorgeben, kann der nächtliche trans-alpine Transport von Luftmassen auch die Luftqualität der atmosphärischen Grenzschicht im Schweizer Mittelland beeinflussen. Dies wurde für Tänikon, eine ländliche Station im Osten des Schweizer Mittellands gezeigt.
Chapter 1

Introduction

The larger scale impact of human activities on air quality started with the beginning of the Industrial Revolution at the end of the 18th century. Severe episodes of air pollutants were reported from London and its surroundings caused by the increasing use of coal (Brimblecombe, 1987). Especially the fast industrial development during the last century resulted in substantial problems regarding the air quality in many parts of the world. Human beings influence the atmospheric composition by diverse anthropogenic activities like the combustion of fossil fuels for domestic and industrial usage, traffic, and biomass burning. Despite substantial efforts to reduce the emissions of various pollutants in the last decades, the problem of air pollution is still a challenging task.

Ozone (O$_3$), nitrogen dioxide (NO$_2$), and fine particles (usually measured as PM10 or PM2.5 (i.e. particles with aerodynamic diameters smaller than 10 or 2.5 $\mu$m, respectively)) are among the pollutants that most frequently exceed the air quality standards in the industrialized world at the present time. O$_3$ is a so-called secondary pollutant without any primary emissions. It is an important air quality issue due to detrimental health effects on humans (Brunekreef & Holgate, 2002) and plants (Fuhrer et al., 1997). Fine particles are predominantly of secondary origin. Dockery et al. (1993) and Laden et al. (2000) showed in epidemiological studies that PM2.5 particles can lead to an increased mortality rate. Strategies to reduce ozone and fine particles are difficult to develop and to apply due to a complex system of chemical reactions (see Sections 1.2.1 and 1.2.3). Volatile organic compounds (VOCs) play a key role in tropospheric chemistry by producing secondary organic aerosols and by forming O$_3$ in the presence of sunlight and catalyzed by nitrogen oxides NO$_x$ (NO$_x$ = NO$_2$ + NO). Haagen-Smit (1952) already found in the 1950s in his studies related to the Los Angeles smog that VOCs and NO$_x$ are the precursors of O$_3$ in ambient air. VOCs include all species of vapor-phase atmospheric organics (Seinfeld & Pandis, 1998). On a global scale, VOCs are predominantly of natural origin. Guenther et al. (1995) estimated an annual global nonmethane VOC flux of 1150 Tg yr$^{-1}$ primarily composed of isoprene.
Chapter 1. Introduction

(44%) and monoterpenes (11%). Global anthropogenic nonmethane VOC emissions are rated to be 51 Tg yr\(^{-1}\) from biomass burning and 98 Tg yr\(^{-1}\) from other anthropogenic sources (MÜLLER, 1992). In non-rural areas, anthropogenic activities can provide the largest VOC sources and can lead to enhanced hydrocarbon levels in the boundary layer of the urban atmosphere (RAPPENGLÜCK & FABIAN, 1999; BORBON ET AL., 2002) even if in some urban areas the biogenic emissions cannot be neglected with respect of photochemical smog formation (CHAMEIDES ET AL., 1988). It was estimated that approximately 23% of the total VOC emissions can be attributed to biogenic sources in Switzerland at the beginning of the 1990s (ANDREANI-AKSOYOGLU & KELLER, 1995).

Biogenic VOCs can play an important role in regional photochemistry and ozone formation by reducing the OH concentration in clean air masses and increasing the peroxy radical concentration that results in an imbalance in the classic photostationary steady state (FEHSENFELD ET AL., 1992; TRAINER ET AL., 1987). Biogenic VOCs represent an interesting group of species as they cannot be reduced through emission controls. Therefore, rising attention was given to the emissions of biogenic VOCs and their oxidation processes in the last years. Anthropogenic VOCs are caused by combustion processes, the production, treatment, storage, and distribution of fossil fuels, solvent use, and industrial production processes. Incomplete combustion processes release mostly hydrocarbons (alkanes, alkenes, aromatics), whereas organic solvents and their vapors can also contain considerable amounts of oxygenated hydrocarbons (FRIEDRICH & OBERMEIER, 1999). Especially aromatic compounds are of particular interest due to their large abundance in motor vehicle emissions, their role in the ozone and aerosol formation (SEINFELD & PANDIS, 1998), and their adverse health effects. Furthermore, benzene, one of the most abundant aromatics, is rated as a human carcinogen.

Most tropospheric NO\(_x\) is emitted as nitrogen monoxide (NO). But within minutes, NO photochemically equilibrates with nitrogen dioxide (NO\(_2\)) (see Section 1.2.1). The most important sources of NO in the boundary layer are every kind of combustion process like vehicle emissions and fossil-fueled power plants as well as emissions due to anaerobic processes in soils, and natural fires (ATKINSON, 2000, and references therein). Lightning and the transport from the stratosphere are considerable free tropospheric NO\(_x\) sources (IPCC, 2001).

Many processes determine the concentrations of the primary and secondary pollutants in the atmospheric boundary layer. Besides the emission sources of the primary pollutants, chemical processes like the photooxidation of VOCs that influence the degradation and production of certain species, and dynamical processes like vertical and horizontal mixing and dispersion play a major role. However, also long-range transport like intercontinental transport or transport across mountain ridges like the Alps can influence the concentrations of less reactive species. These are the main topics that are addressed within this thesis.
1.1 Overview of the thesis

The core of the thesis consists of four papers that were part of the projects COCA (Characterization of Organic Compounds in the Atmosphere), FORMAT (Formaldehyde as a Tracer of Oxidation in the Troposphere), and CHAPOP (Characterization of High Alpine Pollution Plumes) projects. In addition, a Chapter discussing reaction chamber results is included that is not submitted but that is the basis for a future paper in a peer-reviewed journal.

Chapter 2 reports findings on the performance characteristics of a Proton Transfer Reaction Mass Spectrometer (PTR-MS) and describes a critical study of several performance aspects of the instrument. This work was done within the scope of the COCA project that aimed at the measurements of a comprehensive dataset of reactive VOCs and their most important gaseous oxidation products. Two new instruments were tested, characterized, and implemented, and were rated as a valuable tool to gain extensive datasets. This Chapter is submitted to the International Journal of Mass Spectrometry. A second paper I co-authored (not included in this thesis) within the COCA project is also submitted to the International Journal of Mass Spectrometry (AMMANN ET AL., 2003). It is written by the colleagues from the Swiss Federal Research Station for Agroecology and Agriculture more in terms of applications for measurements of biogenic organic compounds.

Chapter 3 describes the laboratory investigation of photooxidation processes in a 1,3,5-trimethylbenzene/NOx system. Various experiments were performed under controlled conditions in a 27 m³ reaction chamber at the PSI. The main focus was to study the formation of secondary organic aerosols from gaseous precursors. The investigation of the formation of aerosol particles, their growth and aging was done in collaboration of PSI and ETH in Zurich. The main emphasis of my work was the monitoring of the organic educts and their oxidation products with the PTR-MS. In addition, box model simulations were performed to get a better insight into the photooxidation chemistry. Finally, the measurements also provided a dataset to validate the model. A publication that arose from these reaction chamber experiments reporting for the first time the identification of polymers as a major component of secondary organic aerosols (not included in this thesis) and including my contribution is published in Science (KALBERER ET AL., 2004).

Chapters 4 and 5 comprise two publications about field campaigns in the Po Basin. Measurements during the FORMAT campaigns as well as data from a former campaign at the same sampling sites and data from a monitoring network of the Lombardy region were used to elucidate the complex VOC emission patterns and the role of meteorology in the Po Basin that lead to observed time series. In-depth analyses allowed for distinguishing different processes and to relate VOC changes to chemical or dynamic mechanisms. Chapter 4 deals with anthropogenic VOCs and focuses on various emission patterns during different periods. Biogenic species and their fate in the atmosphere are investigated in Chapter 5. Both Chapters are
submitted to the Journal of Atmospheric Chemistry.

The fourth paper (Chapter 6) describes the transport of secondary pollutants from the Po Basin to elevated sampling sites in Southern Switzerland, a phenomenon that was observed in Ticino during the CHAPOP field campaign. Perennial time series of ozone south and north of the Alpine crest were used to generalize the findings for the southern part of Switzerland, and to investigate the impact of polluted air masses of the Po Basin on elevated air layers north of the Alps. Finally, the impact on the air quality on the Swiss Plateau was assessed and the additional number of violations of the Swiss national air quality standard for ozone due to southerly advection was estimated for a station in the boundary layer of the Swiss Plateau. Further results of the CHAPOP campaign including my contribution are related to the vertical mass exchange within deep Alpine valleys and are published in Atmospheric Chemistry and Physics (Henne et al., 2004). A publication related to the effects of the traffic emissions in several heights above the valley bottom is submitted to Atmospheric Environment (Kalberer et al., 2003) (both publications not included in this thesis).

1.2 Background

1.2.1 Ozone formation in the planetary boundary layer and the role of VOCs

In the middle of the 19th century, the ozone molecule was discovered by C. F. Schönbein. He performed the first measurements of ozone in the atmosphere and developed the so-called Schönbein method using a treated paper strip and utilizing \( O_3 \) as an oxidizing agent (Kley et al., 1988). Unfortunately, this method only produces semi-quantitative results.

Photostationary steady-state

Ozone is formed in the atmosphere exclusively via the reaction of molecular oxygen with an oxygen atom

\[
O_2 + O + M \xrightarrow{k_1} O_3 + M
\]  

where \( M \) stands for a third molecule like \( N_2 \) or \( O_2 \) that takes up the excess vibrational energy. In the troposphere, atomic oxygen is produced by the photolysis of nitrogen dioxide (\( NO_2 \)) at wavelengths < 424 nm:

\[
NO_2 + h\nu \xrightarrow{j_{12}} NO + O
\]

Nitrogen monoxide (NO) reacts fast with \( O_3 \)
\[ O_3 + NO \xrightarrow{k_{1.3}} NO_2 + O_2 \] (1.3)

that regenerates NO\(_2\). Adding reactions 1.1 to 1.3 results in a zero cycle that produces no net O\(_3\). Reaction 1.1 is very fast so that basically every oxygen atom immediately reacts to O\(_3\). Therefore, the rate determining reaction for the O\(_3\) production is the generation of atomic oxygen. Assuming steady state (ss) conditions the O\(_3\) concentration can thus be calculated by

\[ [O_3]_{ss} = \frac{j_{1.2}[NO_2]}{k_{1.3}[NO]} \] (1.4)

Equation 1.4 is the so-called (classic) photostationary steady state relation. The O\(_3\) concentration depends only on the ratio of NO\(_2\) to NO. However, at many rural sites, the O\(_3\) values in the afternoon are much higher than predicted from NO\(_x\) concentrations. Other reactions than the reactions mentioned above have to play a determining role.

### 1.2.2 Ozone formation under the presence of VOCs

According to equation 1.4, every process that transforms a NO molecule to a NO\(_2\) molecule without consuming O\(_3\) leads by the subsequent photolysis of NO\(_2\) to an increase of the O\(_3\) concentration. Such reactions that inter-convert the NO\(_x\) species are most of all processes involving hydroxy radicals (HO\(_2\)')

\[ HO_2 + NO \rightarrow OH + NO_2 \] (1.5)

and organic peroxy radicals (RO\(_2\)')

\[ RO_2 + NO \rightarrow RO + NO_2 \] (1.6)

These radicals are mainly produced in the troposphere as intermediates in the photochemical oxidation of VOCs and carbon monoxide. The oxidation of the VOCs is usually initiated by the reaction with radicals, usually the hydroxyl radical (OH'). In the lower troposphere, these radicals are either produced via the photolysis of O\(_3\) (\(\lambda < 310\) nm)

\[ O_3 + h\nu \rightarrow O_2 + O(1D) \] (1.7)

and the subsequent reaction with H\(_2\)O

\[ O(1D) + H_2O \rightarrow 2OH' \] (1.8)

or are generated by the photolysis of formaldehyde (HCHO) and higher aldehydes, nitrous acid (HONO) or hydrogen peroxides (H\(_2\)O\(_2\)). Figure 1.1 illustrates schematically the further reactions mechanism. As soon as the VOC oxidation is
initiated, organic radicals (RCH$_2$(OH)) and via the subsequent reaction with O$_2$
peroxy radicals (RCH$_3$O$_2$) are formed. When nitrogen monoxides are present, the
peroxy radicals react with NO to NO$_2$ and oxy radicals (RCH$_2$O$^•$). These oxy rad-
icals are reacting with O$_2$ and forming aldehydes and hydroperoxy radicals (HO$_2$).
Hydroperoxy radicals react again with NO and form OH radicals. The aldehy-
des are either forming OH-radicals via photolysis or react in a sequence similar to
the initially described VOCs. This oxidation mechanism consequently can change
the NO$_2$ to NO ratio to higher values and can therefore be responsible for a net
ozone production. The radical chain can be terminated either by recombination
reactions of radicals and production of hydrogen peroxides (H$_2$O$_2$) or organic perox-
ydes (RCH$_2$OOH) under low NO$^x$ conditions or by the reaction of hydroxyl radicals
with NO$_2$ that leads to a formation of nitric acid (HNO$_3$) during conditions with
high NO$^x$ concentrations. HNO$_3$ is removed from the troposphere either by wet
and dry deposition or by adsorption on or reaction with tropospheric aerosols. Dry
deposition can be also an important sink for O$_3$. For a more detailed description
Exemplarily, the photooxidation of 1,3,5-trimethylbenzene is elaborately
discussed within the Chapter of the reaction chamber experiments (see Chapter 3).
1.2. Background

In brief, this efficient mechanism with the VOCs as the fuel and the nitrogen oxides as the catalysts (as schematically illustrated in Figure 1.1) can generate large amounts of O₃, well above the national air quality standards. Due to the ozone titration with NO (reaction 1.3) and the ceasing photochemical production at night, O₃ levels between sunset and sunrise can be massively diminished in areas with considerable NO sources (e.g. urban areas). Therefore, highest O₃ concentrations are usually not found close to the anthropogenic sources but downwind of polluted metropolitan regions. Especially slow moving high-pressure systems accompanied with cloudless and warm conditions and low wind speeds induce so called 'ozone episodes'. O₃ concentrations can rise within several days until these episodes are often terminated by a passing front that advects cooler and cleaner air masses and subsequently a drop of the O₃ concentrations. Figure 1.2 shows an example of such an episode observed during the FORMAT campaign in 2003.

Nighttime chemistry

After sunset the photolysis reactions that initiate the radical chain reactions are stopped. However, during the night reactions of VOCs with the nitrate radical (NO₃) can become relevant. NO₃ is produced via the reaction

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad (1.9)
\]

An equilibrium is usually reached within circa 1 minute between NO₂, NO₃ and

![Figure 1.2: Time series of ozone, global radiation, and temperature at Verzago (northern Italy) during the FORMAT campaign in 2003.](image-url)
dinitrogen pentoxide ($N_2O_5$) (Seinfeld & Pandis, 1998):

$$NO_2 + NO_3 \xrightleftharpoons[M]{M} N_2O_5$$

(1.10)

During daytime NO$_3$ photolyzes to NO ($\lambda < 595$ nm)

$$NO_3 + h\nu \rightarrow NO + O_2$$

(1.11)

or NO$_2$ ($\lambda < 586$ nm)

$$NO_3 + h\nu \rightarrow NO_2 + O$$

(1.12)

leading to a lifetime of around 5 seconds and sub-ppt mixing ratios. During the night NO$_3$ photolysis does not occur and the reactions with NO

$$NO_3 + NO \rightarrow 2 NO_2$$

(1.13)

and with VOCs (especially alkenes) via an electrophilic addition of NO$_3$ to the double bond are the main NO$_3$ sinks. Nighttime mixing ratios are usually clearly below 100 ppt but can rise up to 350 ppt in polluted areas (Stroud et al., 2002; Geyer et al., 2001; Finlayson-Pitts & Pitts Jr., 2000, and references therein). Nighttime chemistry processes can be of major importance as they determine the starting conditions for next day’s O$_3$ formation.

### 1.2.3 Secondary aerosol formation

The photochemical processes leading to the gas-phase oxidation of VOCs described in Section 1.2.1 also often favor the production of secondary organic aerosols (SOA). Decreased vapor-pressures and increased water-solubilities as compared with the precursor organic compound are responsible for the gas-particle partitioning (Griffin et al., 2003). The subsequently formed secondary aerosol is generated either by nucleation to produce new particles or droplets, or by condensation onto already existing particles. In the last years, especially the chemical processes leading to low-volatility organic oxygenates and their role in the formation of SOA attracted increased attention (e.g. Wang et al., 1992; Odum et al., 1996; Forstner et al., 1997a; Hoffmann et al., 1997; Forstner et al., 1997b; Kalberer et al., 2000; Jang & Kamens, 2001). Carboxylic acids, aldehydes, ketones, alcohols, and nitrates are the oxidation products with the most reduced volatility (Jenkin & Clemitshaw, 2000) and are therefore the most important intermediates concerning the SOA formation. Especially biogenic hydrocarbons like monoterpenes (Hoffmann et al., 1997; Inuma et al., 2004) and isoprene (Claeys et al., 2004) are known to be able to form SOA, but also hydrocarbons of anthropogenic origin like aromatics contribute substantially to their formation (Jang & Kamens, 2001; Cocker et al., 2001).
1.2. Background

Several SOA modules have been developed that can be incorporated into three-dimensional air quality models. But current gas-aerosol thermodynamic models for organic atmospheric species do not have the same level of sophistication as those for inorganic species because of the large number of different organic species and the theoretical challenges due to complex organic-water mixtures (Pun et al., 2002). Comparisons of different models resulted in predicted SOA concentration that varied by a factor of 10 and more, most of all due to different partitioning parameters (Pun et al., 2003). Sensitivity studies by Koo ET AL. (2003) showed that the SOA concentrations are highly dependent on the saturation concentrations and the equilibrium gas mixing ratios. Therefore, more experimental data are needed to improve the knowledge of the driving processes of the SOA formation.

1.2.4 Long-range transport of air pollutants

Even if the enhanced concentrations of the secondary pollutants are most of all a local problem, the pollutants can be transported with the prevailing wind over long distances. Some publications investigated the long-range ozone transport from Asia to the United States (Jacob et al., 1999) and the transatlantic transport between Europe and the USA (Li et al., 2002). Jacob et al. (1999) reported an expected increase of O$_3$ due to a tripling of the Asian anthropogenic emissions in the eastern USA and in the western USA of 2-6 ppb and 1-3 ppb, respectively. According to Li et al. (2002), the possible impact of the American outflow of ozone and its precursors could contribute in continental Europe on average 2-4 ppb to surface ozone.

These studies illustrate that even if high smog episodes are most of all a local problem of the densely populated and highly industrialized areas and their surroundings, attempts to mitigate secondary air pollutants have to be implemented on a regional or even on a continental scale. Measurements and simulations within the scope of the Heilbronn Ozone Experiment dealing with the reduction of ozone due to short term local scale emission reductions showed that such interventions can considerably reduce the primary pollutants but resulted in a negligible effect regarding the peak ozone levels (Moussiopoulou et al., 1997). Concerted large-scale efforts have to be initiated. For Switzerland, the countries that influence the air quality most due to the import of pollutants with the frequently prevailing westerly winds are France, Germany, and Italy (Simpson et al., 1997). Whereas Germany impacts especially the Northern part of Switzerland, the emissions in Italy can result in enhanced pollution levels in Southern Switzerland (Staffelbach et al., 1997). But under certain conditions, even air pollution transport across the Alps can contribute to enhanced secondary pollutant levels (see Section 1.2.5 and Chapter 6).
1.2.5 Transport within and above mountainous terrain

Deep alpine valleys are known to act as efficient ‘air pumps’ that transport air masses and air pollutants upward during daytime (Henne et al., 2004; Carnuth et al., 2002). Figure 1.3 shows a schematic of the daytime atmospheric structure and vertical transport in and above deep Alpine valleys. These air pumps can inject pollutants that are released within the Alpine region (as for example small particles from the motor vehicles on the major trans-Alpine traffic routes in the Leventina and the Mesolcina valley (Henne et al., 2004)) into air masses up to 4 km asl but impede during daytime the exchange of air masses of the southern pre-Alps (e.g. the often highly polluted Po Basin) and the northern pre-Alpine region (e.g. the Swiss Plateau).

During the night, the situation is different as in the typical deep Alpine valleys the katabatic (down-valley) winds are usually developed in the lowest approximately 500 m above the valley floor. As illustrated in Figure 1.4, synoptically driven winds (driven by air pressure gradients) dominate the air flow above the katabatic winds and may lead to an air mass exchange within the residual layers north and south of the Alpine crest. The residual layer reflects an elevated remaining portion of the daytime boundary layer. The trace gas concentrations in the (nocturnal) residual layer are of specific interest as they determine the initial conditions for the next day’s photochemical processes.

1.3 Proton Transfer Reaction Mass Spectrometry

Proton Transfer Reaction Mass Spectrometry (PTR-MS) is a rather novel technique for measuring VOCs in the atmosphere. In the 1990s, scientists at the University
of Innsbruck, Austria developed the PTR-MS system as a combination of chemical ionization and the swarm technique of flow-drift-tube type (Hansel et al., 1995; Lindinter et al., 1998). The chemical ionization system is based on proton transfer reactions that cause a soft ionization with only little fragmentation. Usually, $\text{H}_3\text{O}^+$ ions generated by a hollow cathode discharge are used as primary ions. Subsequently, they enter the drift tube that is continuously flushed with the air to be analyzed. There, the proton transfer takes place (see Figure 1.5). $\text{H}_3\text{O}^+$ ions are a suitable proton donor when air samples with a variety of volatile organic compounds have to be analyzed. Most of the common constituents in the air like $\text{N}_2$, $\text{O}_2$, Argon, CO$_2$, and CH$_4$ have lower proton affinities than H$_2$O so that the $\text{H}_3\text{O}^+$ ions do not undergo reactions with these species. As a consequence, no buffer gas in the drift tube is needed as the air can be used as the buffer gas itself, resulting in high concentrations of the trace gases in the drift tube and a high sensitivity of the instrument. As long as the proton transfer reactions of the primary ions and the reaction partners are exothermic, they are unexceptionally fast with rate coefficients identical to the collisional limiting values for non-polar reactants (Lindinger, 1986a), and the capture rate constants (Chesnavich et al., 1980; Su & Chesnavich, 1982) or the average dipole orientation constants (Su & Bowers, 1973, 1975) in case of polar species (see Section 1.3.3). The reaction rate constants can be calculated according to the different theories so that the concentrations of the certain VOCs could be theoretically derived from the measurements without any calibration limited by the uncertainty of the reaction rate constants of $\pm$ 20% (Hansel et al., 1999). However, as the reaction rate constant cannot be calculated for all species, the settings of the instrument influence the performance
of the instrument and the ionization is not completely non-dissociative for some species, an in-depth characterization of the PTR-MS and a periodical calibration are necessary (see Chapter 2). A compilation of the theoretical background to calculate the concentrations of the respective VOCs are compiled in the following subsections. The required input data for all calculations are the instrument specific parameters $U_{\text{drift}}$, the voltage present at the drift tube, $p_{\text{drift}}$, the pressure in the drift tube, and $T_{\text{drift}}$, the temperature in the drift tube. For more details see also Section 2.2.1.

### 1.3.1 Calculation of the reaction time $t$

The ratio of the electric field strength $E$ to the buffer gas density $N$ has to be known for calculating the reaction time $t$ in the drift tube that is identical with the residence time of the primary ions in the drift tube. $E/N$ can be calculated according to the following equation

$$\frac{E}{N} = \frac{U_{\text{drift}}}{T_{\text{drift}}} \frac{273.15K}{\frac{l_{\text{drift}}}{N_0 \, \frac{273.15K \, p_{\text{drift}}}{\text{latm}}}}$$

where $l_{\text{drift}}$ is the length of the drift tube. The buffer gas density $N$ denotes the number of molecules per cm$^3$ in the drift tube. It is calculated by a temperature and
1.3. Proton Transfer Reaction Mass Spectrometry

\[ y = 7 \times 10^{-12} x^5 - 5 \times 10^{-9} x^4 + 1 \times 10^{-6} x^3 - 9 \times 10^{-5} x^2 + 0.0013 x + 2.7562 \]

![Graph](image_url)

Figure 1.6: Experimental data of the reduced mobility of H$_3$O$^+$ ions in N$_2$ as a function of E/N. Data taken from Ellis et al. (1978).

The pressure correction of \( N_o \) (\( N_o = 2.687 \cdot 10^{19} \text{ cm}^{-3} \)) that is the number of molecules per cm$^3$ under standard temperature and pressure (0 °C and 1 atm). E/N is usually specified in Townsend (Td; 1 Td = 10$^{-17}$ cm$^2$ V$^{-1}$ s$^{-1}$). On the one hand, E/N has to be chosen high enough to avoid strong clustering, but on the other hand, the ratio has to be low enough to minimize the occurrence of fragment ions. The knowledge of E/N is also necessary for the calculation of the reduced mobility \( \mu_o \) (the mobility under conditions of \( p = 1 \text{ atm} \) and \( T = 273 \text{ K} \)) of the H$_3$O$^+$ ions in the drift tube. An experimental determination of the reduced mobility \( \mu_o \) of H$_3$O$^+$ ions in N$_2$ shows a dependence of \( \mu_o \) on E/N (Ellis et al., 1978) (see Figure 1.6). A pressure and temperature correction has to be done to receive the mobility \( \mu \) of the H$_3$O$^+$ ions in the drift tube.

\[
\mu(T_{\text{drift}}, p_{\text{drift}}) = \mu_o \cdot \frac{1 \text{ atm}}{p_{\text{drift}}} \cdot \frac{T_{\text{drift}}}{273K} \tag{1.15}
\]

The drift velocity \( \nu_{\text{drift}} \) is defined as the product of mobility \( \mu \) and the electric field strength \( E \).

\[
\nu_{\text{drift}} = \mu \cdot E \tag{1.16}
\]

Finally, the residence time of the primary ions in the drift tube \( t_{\text{drift}} \) is given by

\[
t_{\text{drift}} = \frac{t_{\text{drift}}}{\nu_{\text{drift}}} \tag{1.17}
\]

The residence time of the primary ions is much shorter than the residence time of the reactants. Therefore, the assumption
is absolutely justifiable. Figure 1.7 shows t-values for a drift tube conditions between 2 and 2.5 mbar and 283 and 333 K. For conditions considerably different to the standard operational settings, the residence time in the drift tube can deviate significantly from the (mean) value given by the manufacturer of 105 μs. A calculation is thus recommended for the particular conditions used during the measurements.

1.3.2 Calculation of the effective temperature in the drift tube $T_{eff}$

For calculating the reaction rate constants, it is first of all necessary to calculate the mean kinetic energy of the drifting ions in the drift tube, given by

$$KE_{ion} = \frac{3k_B T_{drift}}{2} + \frac{M_{buffer} v_{drift}^2}{2} + \frac{M_{ion} v_{drift}^2}{2}$$

where $k_B$ is the Boltzmann constant and $M_{buffer}$ and $M_{ion}$ are the masses of a single buffer gas particle and an ion, respectively (LINDINGER ET AL., 1998). As discussed by McFARLAND ET AL. (1973) and LINDINGER (1986b), it is mandatory for the ion-molecule reactions in the drift tube to know the center-of-mass kinetic energy $KE_{cm}$ for an ion-neutral pair that is given by
1.3. Proton Transfer Reaction Mass Spectrometry

\[ KE_{cm} = \frac{M_{VOC}}{M_{\text{ion}} + M_{VOC}} \cdot (KE_{\text{ion}} - \frac{3k_BT}{2}) + \frac{3k_BT}{2} \]  

(1.20)

where \( M_{VOC} \) is the mass of a certain volatile organic compound (VOC) that acts as a reactant. Using the relation for the thermal energy, it is possible to calculate an effective temperature \( T_{\text{eff}} \) in the drift tube by

\[ T_{\text{eff}} = \frac{2KE_{cm}}{3k_B} \]  

(1.21)

For typical conditions in the drift tube of the PTR-MS as \( U_{\text{drift}} = 600 \text{ V}, \ p_{\text{drift}} = 2 \text{ mbar}, \) and \( T_{\text{drift}} = 298 \text{ K}, \) \( T_{\text{eff}} \) is around 1500 K for characteristic VOCs measured in ambient air.

1.3.3 Calculation of the reaction rate constants \( k_L, k_{ADO}, \) and \( k_{cap} \)

Different theories are available to determine the rate coefficients for ion-molecule reactions. The simplest approach (suitable for non-polar species) is the Langevin theory that results in the Langevin reaction rate coefficient \( k_L \) (LINDINGER, 1986a)

\[ k_L = 2\pi e \left( \frac{\alpha}{M_r} \right)^{1/2} \]  

(1.22)

where \( e \) is the elementary charge, \( \alpha \) is the polarizability, and \( M_r \) is the reduced mass that is defined by

\[ M_r = \frac{M_{\text{ion}} \cdot M_{VOC}}{M_{\text{ion}} + M_{VOC}} \]  

(1.23)

It is noteworthy that the temperature is not considered in \( k_L \). Consequently, \( k_L \) is not affected by \( T_{\text{drift}} \) or \( T_{\text{eff}} \).

The effect of a permanent dipole of the reactant is taken into account by the so-called average-dipole-orientation (ADO) theory developed by SU & BOWERS (1973). A permanent dipole results in a larger capture rate coefficient. \( k_{ADO} \) can be calculated from

\[ K_{ADO} = 2\pi e \left( \frac{1}{M_r} + C \mu_D \frac{2}{\pi k_BT} \right)^{1/2} \]  

(1.24)

where \( C \) is a parameter that takes into account how effective the charge is locking in the dipole. \( \mu_D \) is the permanent dipole and \( T \) is the temperature of the drift tube or the effective temperature depending if the electric field is considered. \( C \) can be calculated theoretically and depends only on the ratio \( \mu_D/\alpha^{1/2} \). \( C \)-values are in the range between 0 and 1 and are given by SU & BOWERS (1973, 1975).
The third theory is based on a parameterization of the ion-molecule collision rate constant by trajectory calculations made by Chesnavich et al. (1980) and Su & Chesnavich (1982). A combined variational transition state theory/classical trajectory study was performed to determine the thermal energy ion-polar molecule capture collisions. They have shown that the ratio of the thermal capture rate constant \( k_{\text{cap}}(T) \) to the Langevin capture rate coefficient \( k_L \) depends on only two reduced parameters:

\[
\frac{k_{\text{cap}}(T)}{K_L} = K_{\text{cap}}(T_R, I^*)
\]  

(1.25)

\( T_R \) is defined as \( T_R = 2\alpha k_BT/\mu_D^2 \) and \( I^* \) as \( I^* = \mu_D I/\alpha e M_r \) where \( I \) is the moment of inertia of the neutral. The results of around 3000 calculated trajectories for each combination of \( T_R \) and \( I^* \) are précised in an empirical fit of the trajectory curve:

\[
K_{\text{cap}} = \begin{cases} 
0.4767x + 0.6200 & \text{for } x \geq 2 \\
\frac{(x+0.5099)^{1/2}}{10.526} + 0.9754 & \text{for } x \leq 2 
\end{cases}
\]  

(1.26)

where \( x \) is defined as \( x = 1/(T_R)^{1/2} = \mu_D/(2\alpha k_BT)^{1/2} \). Similar to \( k_{\text{ADO}} \), \( k_{\text{cap}} \) depends on the temperature. It leads to significantly lower results when the effective temperature is used.

The Langevin theory has to be used for molecules without a permanent dipole moment resulting in temperature independent rate coefficients for the compounds. For molecules with a permanent dipole moment, it is mandatory to use either the average-dipole-orientation theory or the more sophisticated variational rate/trajectory theory to calculate the required rate coefficients.

### 1.3.4 Recommendations for using the PTR-MS

When using the average-dipole-orientation theory or the variational rate/trajectory theory, the manufacturer recommended to consider the effective temperature in the drift tube which is significantly higher than the drift tube temperature. The applied voltage of approximately 600 V at the drift tube leads to around 5 times higher effective temperatures. This results in up to a factor of 2 smaller \( k_{\text{cap}} \)-values for species with large dipole moments like acetone.

Usually, we used three different 8-component standards including TMB, propene, toluene, \( \alpha \)-pinene and oxygenated VOCs (Apel&Riemer Environmental Inc., Denver, USA) to determine the sensitivity of the instrument. For compounds without an available gas standard, we calculated the mixing ratios of the oxidation products using computed reaction rate constants and corrected the results according to the calibrated sensitivity. We found out that the experimentally determined instrumental sensitivity is more consistent for the whole set of VOCs when using
the drift tube temperature instead of the effective temperature derived according to equation 1.21. Since especially oxygenated VOCs possess high dipole moments, these species are most sensitive to temperature variations leading to considerably lower rate constants and higher VOC concentrations when using the effective temperatures. The use of the drift tube temperature shifted the rate constants and subsequently the VOC concentrations, that usually a more consistent sensitivity has been achieved. Therefore, we recommend in contrast to the manufacturer the use of the drift tube temperature rather than the effective temperature when calculating the respective rate constant.

Despite the large number of publications in the last years not only in atmospheric sciences but also in medical and food research, there is only a very limited number of publications dealing with comparisons of PTR-MS results with alternative and more established methods (Sprung et al., 2001; de Gouw et al., 2003a; Küster et al., 2004) or discussing problems that occur when measuring under changing environmental conditions in the field (Warneke et al., 2001; de Gouw et al., 2003b).

1.4 Laboratory and field studies of this thesis

Laboratory and field studies were conducted to characterize the PTR-MS. An inter-comparison of two PTR-MS instruments measuring ambient air was performed. Humidity and temperature dependencies of the performance characteristics were investigated and several other state of the art techniques (GC-FID, Hantzsch fluorescent method) were used to intercompare the PTR-MS results.

Laboratory studies concerning the photooxidation of selected VOCs in a controlled environment were conducted in the newly built PSI reaction chamber. The PSI reaction chamber consists of a 27 m$^3$ transparent Teflon$^\circledR$ bag mounted in a temperature controlled housing with reflecting walls. Four xenon arc lamps (4 kW each) are used to simulate the solar light spectrum as closely as possible and to mimic natural photochemistry. Primary gas components such as organics, oxides of nitrogen, purified air, and water vapor are flushed into the chamber where they diffuse and mix for 30-45 minutes before turning on the lights. The time series of the gaseous species recorded during the smog chamber experiments using GC-FID and PTR-MS were compared with the model output of the Master Chemical Mechanism (v3) and were used to validate the model. The Master Chemical Mechanism (Jenkin et al., 1997, 2003; Saunders et al., 2003) is a near-explicit mechanism that includes the kinetics of the tropospheric VOC degradation and the production of secondary pollutants.
Field measurements were conducted within the CHAPOP and the FORMAT project. Measurements of VOCs, inorganics, and meteorological parameters were performed in summer 2001 at six surface stations in southern Switzerland within the scope of the CHAPOP project. The measurements took place in the Levantina Valley, Ticino, where one of the major trans-Alpine traffic routes runs. The campaign was focused on the vertical mass exchange (Henne et al., 2004) and the effects of the traffic emissions in several heights above the valley bottom (Kalberer et al., 2003). The present work (see Chapter 6) was based more on a climatological perspective and focussed on the transport of polluted air masses from the Po Basin towards southern Switzerland and across the Alps, and the effects on the air quality on the Swiss Plateau. It is already known that the Ticino region is influenced by polluted air originating from the Po Basin due to orographically induced wind system, especially during the day in summer (Staffelbach et al., 1997). Elevated measurement sites located above the diurnal mountain wind system can be substantially influenced by the Po Basin even during the night when synoptic winds come from southerly directions (see Figure 1.8 that shows measurements at the San Bernardino Pass from the VOTALP Mesolcina valley campaign in 1996 (Furger et al., 2000)). Mixing ratios above 100 ppb were
only observed in coincidence with southerly winds during the night. The up-valley winds during daytime of the diurnal mountain wind system were not strong and persistent enough to transport polluted air masses to the crest at the northern end of the Mesolcina valley so that synoptically driven southerly wind in the night was necessary that the air masses could reach the measurement site.

In summer 2002 and autumn 2003, two measurement campaigns within the FORMAT project were performed. Measurements of VOCs, inorganics, and meteorological parameters took place in the Po Basin at two measurement sites: at an urban station about 5 km north of downtown Milan and at a semi-rural site around 35 km north of the city center. In the Po Basin and the greater Milan area highest O₃ concentrations in Europe are measured (Prévôt et al., 1997; Dommen et al., 2002). Prévôt et al. (1997) reported mixing ratios of up to 185 ppb 4 to 5 hours downwind of Milan. Thiellmann et al. (2002) found mixing ratios of nearly 200 ppb 35 km north of Milan. The above mentioned topographically induced diurnal wind system influences the wind regime nearly in the whole Po Basin so that the Milan photooxidant plume moves generally to the north where the semi-rural measurement site was located. The present work focussed more on local sources, photochemical processes, and local sinks that influence the diurnal VOC patterns at the semi-rural site (see Chapters 4 and 5). Several results from measurements in 1998 within the scope of the PIPAPO campaign (Neftel et al., 2002; Grüebler, 1999) at the same sampling sites were included in the analysis of the results from the FORMAT campaigns.

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Chapter 2

Performance Characteristics of a Proton Transfer Reaction Mass Spectrometer Derived From Laboratory and Field Measurements

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Abstract Volatile organic compounds (VOCs) play an important role in the formation of ozone and aerosols in the atmosphere. In an increasing number of field campaigns the proton-transfer-reaction mass spectrometer (PTR-MS) has proven to be a useful and fast tool for measuring VOCs and studying the relevant atmospheric processes. This work describes laboratory and field measurements with two different versions of the PTR-MS and presents important instrument specific features. The temperature stabilization and the change of the gasket material in the newer version significantly improved the performance of the instrument, as demonstrated by periodical background measurements under field conditions. The investigation of the mass discrimination illustrated the necessity of an elaborate verification. The humidity dependence of benzene was substantially lower than in former studies, which used higher drift tube pressures, but it is still higher than predicted by a simple dimer/monomer equilibrium model. An instrument comparison with a fluorescent technique was performed for formaldehyde and showed differences between pure formaldehyde calibration gases and complex ambient air samples. An inter-comparison of two PTR-MSs measuring ambient air yielded satisfactory results after

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calibration for most of the considered masses. Comparing PTR-MS and gas chromatograph measurements of aromatic compounds revealed a good agreement for conditions of fresh anthropogenic emissions. In photochemically aged air, many masses detected by the PTR-MS are not only influenced by anthropogenically and biogenically emitted but also oxidized VOCs.

2.1 Introduction

The proton transfer reaction mass spectrometer (PTR-MS) was developed by Lindinger and co-workers at the University of Innsbruck, Austria (LINDINGER et al., 1998a). A multitude of PTR-MS related publications have appeared in environmental sciences (e.g. CRUTZEN et al., 2000; HOLZINGER et al., 2000; KARL et al., 2001a), food analysis (e.g. BOSCHETTI et al., 1999; YERETZIAN et al., 2003; MAYR et al., 2003), and medical applications (e.g. LINDINGER et al., 1997; TAUCHER et al., 1997; PRAZELLER et al., 1998; KARL et al., 2001b) within the last years.

Early publications about the PTR-MS claimed that it is not necessary to perform regular calibrations for different volatile organic compounds (VOCs) (LINDINGER et al., 1998a; HANSEL et al., 1995; LINDINGER et al., 1998b; HANSEL et al., 1999) as long as instrument-specific parameters (like the transmission function and the residence time of the primary ions in the reaction chamber) as well as the compound-dependent reaction rate constants for the protonation of these VOCs are known. The rate constants can theoretically be calculated with the aid of empirical relations (GIOMANIS & STEVENSON, 1958; SU & BOWERS, 1973; SU & CHESNAVICH, 1982). HANSEL et al. (1999) estimated the accuracy of the VOC mixing ratio measurements to 30%, mainly caused by the uncertainties of the reaction rate constants, which are up to ± 20%. Other instrument- and configuration-specific experimental effects were not considered relevant. Recent publications postulate a detailed characterization and calibration of the PTR-MS by means of gas standards (WARNEKE et al., 2001; HAYWARD et al., 2002; DE GOUW et al., 2003). However, as the instrument can measure a large amount of different substances and gas standards are not available for all compounds, the concentrations of various compounds still need to be calculated from the count rates according to the theory. Therefore, the assumptions used for the calculation of concentrations need to be checked carefully. This paper presents important characterizations of the instrument concerning the temperature dependence of the background signal, the humidity dependence of the sensitivity and the determination of the transmission function. Furthermore, comparison measurements of ambient concentrations of the PTR-MS with a gas chromatograph and a formaldehyde monitor are shown.
2.2 Experimental

2.2.1 PTR-MS methodology

The PTR-MS instrument (IONICON Analytik GmbH, Innsbruck, Austria) has been described in detail in numerous publications elsewhere (Lindinger et al., 1998a; Hansel et al., 1995; Lindinger et al., 1998b; Hansel et al., 1999; Lindinger & Hansel, 1997; Hansel et al., 1998). Therefore, just a short description is given here. The measuring method is based on a proton transfer reaction of hydronium ions ($H_3O^+$) to compounds with a higher proton affinity than water and subsequent detection of the product ions in a quadrupole mass spectrometer. For investigations of trace components in air, $H_3O^+$ is a suitable proton donor because the primary ions do not react with any of the common constituents in air like nitrogen, oxygen, carbon dioxide, carbon monoxide, methane, and ozone. Most common volatile organic compounds in the atmosphere, excluding the alkanes and small alkenes/alkynes exhibit sufficient proton affinities (NIST, 2003). The proton transfer ionization takes place at relatively low energies and therefore causes only little fragmentation of most of the ion products. However, it can have a considerable effect for some specific compounds like isoprene (Ammann et al., 2003) and the monoterpenes (Tani et al., 2003). A hollow cathode discharge generates $H_3O^+$ and a number of other ions ($H^+$, $O^+$, $H_2^+$, $OH^+$, $H_2O^+$) from pure water vapor. Afterwards the ions pass a source drift region where ions other than $H_3O^+$ are almost completely converted to $H_3O^+$. Subsequently, the $H_3O^+$ ions enter the drift tube that is continuously flushed with the sample air at a pressure of slightly higher than 2 mbar. In the drift tube VOCs are ionized according to the following reaction:

$$H_3O^+ + VOC \rightarrow VOCH^+ + H_2O$$

(2.1)

If the VOCs are present in quantities below a few parts per million, the $H_3O^+$ ions do not decrease significantly such that $[VOC] \gg [H_3O^+] \gg [VOCH^+]$ is valid. The number density of a VOC in the lower ppb range adds up to around $10^8$ molecules cm$^{-3}$ at typical drift tube conditions, the $H_3O^+$ concentration in the drift tube is approximately $10^4$ ions cm$^{-3}$ (A. Hansel, personal communication). The residence time of the air to be analyzed is around 0.1 sec. This results in a VOC decrease due to equation 2.1 of 0.0002% taking into account typical primary ion concentrations and reaction rate constants. Assuming a total VOC loading of 1 ppm and considering a residence time of the ions in the drift tube of around 100 $\mu$s, the proton transfer reaction leads to a $H_3O^+$ ions decay of around 1%. In brief, due to the short reaction time neither the VOCs nor the primary ions decrease significantly due to reaction 2.1. Under these conditions, and taking into account the mass-dependent transmission of the instrument, the number density of a certain compound can be calculated from


\[
[\text{VOC}] = \frac{[\text{VOCH}^+] \cdot \text{trans}([\text{H}_3\text{O}^+])}{\text{H}_3\text{O}^+ \cdot \text{trans}([\text{VOCH}^+]) \cdot k \cdot t}
\]  

(2.2)

where \( t \) is the residence time of the primary ions in the drift tube (typically circa 100 \( \mu \)s), \( k \) is the proton transfer reaction rate constant which corresponds to the ion-molecule capture collisions and \text{trans(...)} is the mass-dependent transmission for the respective ions. \([\text{VOCH}^+]\) and \([\text{H}_3\text{O}^+]\) are taken from the ion signals of the protonated VOC and the primary ion, respectively. Typical count rates of the primary ions are 4 to 5 Mio cps (counts per second). Therefore it is feasible to measure the \(^{18}\text{O}\) isotope of the primary ion (\( \text{H}_3^{18}\text{O}^+; \text{m}/\text{z} 21 \)) to avoid reaching the saturation range and to reduce aging effects of the detector. Due to an isotope ratio \(^{18}\text{O}/^{16}\text{O}\) of 0.20\% (Barker, 1999), the \text{m}/\text{z} 21-signal has to be multiplied by 500 to obtain the primary ion counts. The reaction rate constants can be calculated based on different theories (Su & Bowers, 1973; Su & Chesnavich, 1982; Lindinger, 1986; Chesnavich ET al., 1980). They include an uncertainty of 20\% (Hansel ET al., 1995, 1999). In the following, the Langevin theory (Lindinger, 1986) was used for molecules with an unknown or without dipole moment. For molecules with a permanent dipole moment, the reaction rates were determined according to the parameterizations based on trajectory calculations done by Chesnavich ET al. (1980) and Su & Chesnavich (1982). A secondary electron multiplier detects the primary and the product ions after passing a quadrupole mass spectrometer. The electron multiplier is attached perpendicular to the hollow cathode, the drift tube, and the quadrupole mass spectrometer to minimize the background signal. Photons and fast neutral particles can also trigger a pulse at the electron multiplier. This effect can be suppressed by this perpendicular configuration. An electrostatic field deflects the ions between the quadrupole and the detector. As the deflection is mass-dependent, it influences the transmission in equation 2.2. The transmission is also reduced due to ion losses between the drift tube and the quadrupole. Another approach to derive VOC mixing ratios is based on calibrating the instrument with gas standards and calculating the concentrations by using appropriate calibration factors. But, as the instrument can measure a large amount of different substances and gas standards are not available for all compounds, the determination of the concentrations with equation 2.2 is still needed.

2.2.2 PTR-MS setup

Performance tests and measurements of two instruments are presented in this work. The first has been operated by Agroscope FAL (Federal Research Station for Agroecology and Agriculture) since 2000 and is referred to as the PTR-MS (FAL). The second is a newer version of the instrument, operated by the Paul Scherrer Institut since 2002, denoted as PTR-MS (PSI) hereafter. The PTR-MS (FAL) had a drift tube of 9.5 cm length and 5 cm diameter and was equipped with Viton gaskets.
2.2. Experimental

Until September 2001, ambient air was aspired through a mass flow controller and perfluoroalkoxy (PFA) tubings before entering the drift tube. The mass flow controller was then replaced by a pressure flow controller in a bypass, as it is now standard for this instrument. The newer instrument, the PTR-MS (PSI), is optimized in terms of a faster response, temperature stabilization, and gasket and tubing materials. It is equipped with a drift tube of 9.25 cm length and of 1.4 cm diameter and teflon gaskets. The inlet system and the drift tube of this instrument are kept at a constant temperature of 50 °C to reduce the temperature dependent variations of the background signal. The blank values were measured passing the ambient air through a Supelpure™ charcoal cartridge (Supelco, Bellefonte PA, USA).

2.2.3 Other VOC analyzers

Both mass spectrometers were operated in the laboratory as well as in the field in parallel to other state of the art methods for VOC measurements like gas chromatography for hydrocarbons and a fluorescent technique for formaldehyde.

A commercial Airmotec HC1010 gas chromatograph (ChromatoSud, Saint Antoine, France) was used to measure hydrocarbons between C₄ (hydrocarbons containing four carbon atoms) and C₁₀ (Konrad & Volz-Thomas, 2000). Sample air is pulled through adsorption tubes containing Carbopack B and Carbosieve III. After desorbing, the hydrocarbons are cryofocused using a fused silica capillary packed with Carbopack B and cooled by rapid expansion of CO₂ to -25 °C. Injection onto the chromatographic column proceeds after fast desorption at 350 °C. The stationary phase of the separation column consists of 2.5% phenyl- and 97.5% methylpolysiloxan (BGB Analytik AG, Anwil, Switzerland). A flame ionization detector (FID) is used for detection. The instrument was operated in a mode to obtain concentrations averaged over 30 minutes.

Formaldehyde (HCHO) was continuously measured with the Hantzsch method as described by Kelly & Fortune (1994). HCHO is collected in a glass coil scrubber. The scrubbing solution is mixed with the Hantzsch solution (mixture of acetic acid, acetylacetone and ammonium acetate). A fluorescent derivative is formed from a reaction of formaldehyde with ammonium acetate and acetylacetone in a heated reaction coil. The produced diacetyldihydrolutidine (DDL) is then detected by fluorimetry. The excitation and emission wavelengths are 400 and 510 nm, respectively.

2.2.4 Measurement locations

A field campaign including a comparison of PTR-MS (FAL) and gas chromatograph (Airmotec HC1010) measurements took place in Berne, Switzerland in March 2001. Ambient air was measured on the top of a 15 m high building close to a road with
heavy traffic. The intention of the campaign was an assessment of urban ammonia emissions and their correlation to VOC emissions.

In August and September 2001, the PTR-MS (FAL) was operated in parallel to the formaldehyde monitor for measurements of ambient air within the scope of the CHAPOP (Characterization of High Alpine Pollution Plumes) campaign in the Leventina valley, southern Switzerland. The measurements were performed in a rural environment at 1240 m above sea level and about 500 m above the valley ground where one of the major trans-alpine traffic routes passes by. The aim was to enhance the knowledge of photochemical processes and vertical transport of air pollutants in the high Alpine atmosphere. Further measurements were performed in the Po Basin in Northern Italy in summer 2002 in the framework of the EU project FORMAT (Formaldehyde as a Tracer of Photooxidation in the Troposphere) project. The instruments were located in a semi-rural environment which was sometimes influenced by the plume of Milan. These measurements will be used to investigate the formaldehyde formation processes and the role of formaldehyde in photochemistry.

2.3 Results and discussion

2.3.1 Temperature dependence of the background signal

During the CHAPOP campaign, the PTR-MS (FAL) was located in an air-conditioned trailer. Because of problems with the air conditioning, a significant diurnal variation of the temperature with a daily amplitude up to 14 °C occurred inside the container during some sunny days. The blank values were measured every 3 hours for 30 min. The diurnal patterns of the indoor temperature and the blank values of benzene (m/z 79), C_2-benzenes (m/z 107) and C_3-benzenes (m/z 121) are shown in Figure 2.1. The PTR-MS mass signals were converted to mixing ratios according to equation 2.2. The blank values of all three masses strongly depended on the indoor temperature. Laboratory tests showed that this effect could not be related to a changing efficiency of the charcoal cartridge within the observed temperature range.

The observed temperature and pressure variation from 16 °C to 30 °C and 2.03 mbar to 2.09 mbar affect the residence time of the primary ions in the drift tube by about 2%. The calculated reaction rate constants change only marginally. Therefore, the temperature and pressure dependence of the residence time and the reaction rate constants for the protonation cannot explain the variability.

During the FORMAT campaign, similar problems with the temperature control in the measurement container occurred and the instrument was exposed to diurnal temperature variations of up to 8 °C. These measurements were performed with the temperature stabilized PTR-MS (PSI). No correlation between the indoor
2.3. Results and discussion

Figure 2.1: Indoor temperature and calculated blank value mixing ratios according to equation 2.2 of benzene (m/z 79), C2-benzenes (m/z 107) and C3-benzenes (m/z 121) for a 7-day-period during the CHAPOP field campaign in southern Switzerland.

The background variability is most likely related to impurities in the instrument that are desorbed more efficiently at higher temperatures. It explains the lower variations of the PSI instrument with its temperature controlled drift tube. Besides the temperature stabilization, the change of the gasket material from Viton to Teflon might also have improved the system. GC-PTR-MS measurements performed by WARNEKE ET AL. (2003) showed broad peaks when using Viton gaskets
and sharper peaks when using Teflon. They are attributing this phenomenon to memory effects (adsorption and desorption processes) on the Viton.
2.3. Results and discussion

2.3.2 Mass discrimination

The detection efficiency of the instrument is mass dependent. The mass discrimination of the instrument is influenced by three factors: losses of ions between the drift tube and the quadrupole, mass characteristics of the quadrupole and the deflection between the quadrupole and the SEM. To calculate the mixing ratios, the (mass dependent) efficiency of the detection must be considered. A default curve for the mass discrimination is provided by the manufacturer. A new measurement of the transmission was performed in the following way. The determination of the transmission for mass \(x\) is based on the comparison of the decline of the primary ions (m/z 19 or the protonated water isotope, m/z 21 (H\textsuperscript{18}O\textsuperscript{+})) and the increase of the signal of mass \(x\). To obtain observable signals, an air sample with a high concentration of a species with protonated mass \(x\) has to be fed to the instrument. Based on the characteristics of the instrument, the transmission for a mass between 100 and 110 is usually set equal 1 and the whole transmission curve can be determined relative to this reference by this technique. The transmission can be derived by comparing the decline of the primary ions and the simultaneous increase of the mass \(x\) signal. Before starting the determination of mass discrimination, the primary ion signal was reduced from approximately 4 Mio cps to around 700,000 cps to avoid reaching the saturation of the SEM. Figure 2.3 shows the raw data of

![Figure 2.3: Raw data for determination of the transmission of m/z 33 (methanol), m/z 59 (acetone), m/z 93 (toluene), m/z 101 (acetyl acetone), m/z 107 (xylene), and m/z 121 (trimethylbenzene). m/z 94 (\textsuperscript{13}C-toluene) is added for illustration of the apparent \textsuperscript{13}C-isotopes. One cycle took 5 seconds.](image)
a transmission curve determination experiment.

The measurements were performed with Tedlar gas sampling bags (1 to 4 liter volume, Varian Inc., Palo Alto, CA, USA) filled with selected VOCs at ppm levels. These concentrations were obtained by injection of pure liquid solutions (Fluka Chemie GmbH, Buchs, Switzerland and Merck, Darmstadt, Germany, GC quality ≥ 99.5%). After injecting the compound, the bags were filled with dry synthetic air. Around 1 µl of the pure compound per liter pillow bag volume was injected to yield an appropriate concentration. As the signal of the primary ions is increasing slightly with increasing humidity (as shown later, see Figure 2.6), dry synthetic air was measured between switching the bags. Full scans were conducted to control if potential fragments or dimers could influence the mass discrimination measurements before the experiments. Only species without any significant fragmentation or dimer formation in the drift tube were used. 13C-isotopes were considered for the mass discrimination determination.

The results of several transmission measurements are summarized in Figure 2.4. It is obvious that the experimentally determined curve significantly deviates from the (also experimentally determined) curve given by the manufacturer. Even when the two largest outliers are ignored, the discrepancy between the two different curves can amount up to 25%. The reason for this discrepancy may be attributed to different settings during the measurements, long term drifts, or can be caused by the inaccuracy of a single transmission curve measurement. The error bars indicate the

![Figure 2.4](image-url)  

Figure 2.4: Averaged transmission curve of the PTR-MS (PSI-instrument). The transmission for xylene (protonated mass 107) was set equal 1. The error bars show the standard deviation. Number n specifies the number of measurements.
large scatter between the different measurements. Quadrupole mass spectrometers have often lower sensitivities for heavier ions because heavier ions spend more time in the fringing fields resulting in a larger dispersion of the ions (DAWSON, 1976).

Therefore the low transmission value for mass 153 (protonated camphor) might be explained by the fringing fields. As the use of the other compounds with similar masses failed due to significant fragmentation, it cannot be determined if it is a general characteristic of the PTR-MS or a camphor-specific effect. Full mass scans did not show any significant fragmentation of camphor in agreement with results published by TANI ET AL. (2003). Therefore, a possible fragmentation of camphor can be excluded as a source of error.

Recurring calibrations of the instrument with gas standards over around 10 months also show a variability of nearly ± 30%. If the scatter of the transmission is not related to the method of the determination itself, most of the variability of the calibration could be explained by the changing transmission properties of the PTR-MS. Surprisingly, the transmission curve of the PTR-MS (FAL) shows a smaller scatter (AMMANN ET AL., 2003) although the mass discrimination for both instruments was determined simultaneously with the same bags and the same concentrations. In contrast, the transmission of camphor concordantly shows a similar low value for the PTR-MS (FAL).

Finally it should be mentioned that the knowledge of the transmission is not necessary if a reliable calibration of the mass spectrometer for a certain compound is available. Even the rate constants and the reaction time are ultimately integrated in the calibration factor. But detailed considerations are required for compounds without a reliable calibration gas. Moreover, no investigations about the long-term stability of the transmission curve are available. But measurements by AMMANN ET AL. (2003) at least have shown that the aging of the secondary electron multiplier can mass-dependently affect the amplification of the signal and can consequently influence even the transmission function. Therefore, periodical evaluations of the transmission or calibrations are recommended.

2.3.3 Humidity dependence of the benzene sensitivity

Recently, WARNEKE ET AL. (2001) have shown that the benzene sensitivity is strongly dependent on the humidity of the analyzed air. They attribute the humidity sensitivity to a discrepancy between the measured cluster ion distribution and the actual one in the drift tube. They relate it to a collision induced dissociation (CID) which takes place between the drift tube and the quadrupole. As a consequence, more H$_3$O$^+$ and less H$_3$O$^+$H$_2$O ions are measured because the water clusters dissociate back to the unhydrated form at the end of the drift tube. Benzene does not react with H$_3$O$^+$-(H$_2$O)$_n$ clusters due to a too low proton affinity (WARNEKE ET AL., 2001; SMITH ET AL., 2001).

We performed measurements of the humidity dependence of benzene in the
laboratory (room temperature 23 °C) using a gas standard with 0.75 ppm benzene (BOC Gase GmbH, Stuttgart, Germany), diluted with synthetic air by using two mass flow controllers, and a humidifier (LI-COR LI-610, Lincoln, NE, USA). The PTR-MS (PSI) was operated at $p_{drift} = 2.08$ mbar, $T_{drift} = 323$ K, $U_{drift} = 570$ V, and $E/N = 132.3$ Td conditions. $E/N$ denotes the ratio of the electric field strength $E$ and the buffer gas density $N$.

Figure 2.5 shows the calibration curve for benzene (m/z 79) at 5 different relative humidities. Considering the raw signal of m/z 79 (see the inset in Figure 2.5), no humidity dependence is observable. But, the primary ion signal is slightly changing with relative humidity, as shown in Figure 2.6 including the raw signals of $\text{H}_3\text{O}^+$ (m/z 21) and of the water cluster $\text{H}_3\text{O}^+\text{H}_2\text{O}$ (m/z 37). The $\text{H}_3\text{O}^+$ ion signal as well as the water cluster signal are rising with increasing humidity.

After standardizing the m/z 79 signal to $10^6$ cps $\text{H}_3\text{O}^+$ primary ions, a humidity dependence (shown in the large plot of Figure 2.5) is observed. This humidity dependence is similar but less distinct to that described by Warneke et al. (2001). The measurements presented in this work show a change in the sensitivity between dry and humid conditions of about 16%, whereas Warneke et al. (2001) have detected a change of nearly 130%.

Warneke et al. (2001) have developed a simple model that computes the cluster ion distribution in the drift tube. Using this model, it was possible to

![Figure 2.5: Calibration curve of benzene. The small panel shows the raw signal of m/z 79 (protonated benzene) vs. the benzene mixing ratio in the gas standard at five different relative humidity values. The large panel shows the standardized raw signal of m/z 79 vs. the same x-axis. Standardization is described in the text.](image-url)
explain the dependence of the sensitivity on the humidity. For these studies, the authors have operated the PTR-MS at a drift tube pressure of 2.5 mbar. We performed similar tests with the PTR-MS (PSI) at a drift tube pressure of 2.08 mbar, which is equal to our standard operational conditions and is approximately the default value given by the manufacturer. Model calculations similar to those done by Warneke et al. do predict no cluster formation for a larger range of water concentrations. In contrast to that, we observed a dimer/monomer ratio of 1 to 15% between dry air and 100% humidity. These results are in accordance with another measurement to model comparison done by Hanson et al. (2003) and de Gouw et al. (2003) that also measured higher water cluster fractions than modeled at E/N above 110 Td. The model cannot accurately describe the cluster distribution in the drift tube since the measured distribution depends on the exact conditions in the drift tube and how the ions are extracted from the drift tube into the quadrupole mass spectrometer, the ion source water flow, and pumping characteristics. As seen from Figure 2.6, there is no direct correlation between the measured sensitivity and the water cluster distribution. This can be explained by a less efficient CID at higher relative humidities or by a partly compensating production of water clusters in the jet that occurs due to the pressure drop between drift tube and quadrupole. Similar jets are a common tool for the production of dimers (Coudert et al., 1987).

The biggest change in sensitivity (see Figure 2.5) appeared from absolutely dry to slightly humid conditions. This means that the effect in outdoor measurements should be small, because absolutely dry conditions do not occur in the troposphere.
The slope decreases from 15.4 standardized cps per ppb at 33% relative humidity to 14.6 standardized cps per ppb at 94% relative humidity. Compared to the overall uncertainty of the measurement, this change of 5% can be neglected for many applications. However, it should be emphasized that the effect has to be taken into account if the PTR-MS is calibrated under dry conditions and is operated under humid conditions.

2.3.4 Formaldehyde comparison

The proton affinity of formaldehyde (170.4 kcal/mol) is just slightly higher than that of water (165.2 kcal/mol) (NIST, 2003). Therefore, the reaction of protonated HCHO with water becomes relevant and reduces the sensitivity. HANSEL ET AL. (1997) investigated the H$_3$O$^+$ proton transfer reaction to formaldehyde including the back reaction in a selected ion flow drift tube experiment (SIFT). They measured an energy dependence of the rate constants mainly for the backward reaction. For our conditions of the relative kinetic energy between the reactants (KE$_{cm} = 0.17$ eV), they found a rate constant of $k_f \approx 1.5 \times 10^{-9}$ cm$^3$ s$^{-1}$ for the forward and of $k_b \approx 2.8 \times 10^{-11}$ cm$^3$ s$^{-1}$ for the backward reaction.

We performed a laboratory intercomparison of HCHO with the PTR-MS (FAL) and a formaldehyde (Hantzsch) monitor. Different gaseous formaldehyde concentrations were produced with a permeation source and dilution with zero air. The permeation source was made out of a glass flask filled with para-formaldehyde and closed with a Tedlar film. The source was temperature stabilized at a temperature of 50 °C in an oven integrated in the Hantzsch monitor. The Hantzsch monitor was calibrated by means of an aqueous formaldehyde solution ($\approx 2 \mu$M).

Figure 2.7 shows the results of the HCHO measurements. A linear relation between the data of the two instruments was obtained whereby the PTR-MS (FAL) observed only 21% of the HCHO measured by the Hantzsch monitor. However, the measurement of laboratory air right after this intercomparison resulted in a yield of 38% for the PTR-MS.

The intercomparison with the permeation source was carried out under dry conditions whereas the laboratory air contained some humidity. But this cannot explain the different sensitivity. The backward reaction of protonated HCHO with water should become more distinct under more humid conditions leading to a even lower sensitivity. For a humidity range between 20,000 and 80,000 ppm and $10^4$ primary ions cm$^{-3}$, we predicted sensitivities of 37% to 10%. The higher recovery rate of the PTR-MS during the laboratory air measurement compared to the calibration mixture shows that an interference with some other compounds existing in the laboratory air cannot be excluded. A more detailed discussion follows at the end of the section.

A comparison of formaldehyde measurements in ambient air during the CHAPOP field campaign in southern Switzerland in summer 2001 is shown in Fig-
2.3. Results and discussion

Figure 2.7: Laboratory intercomparison between measurements of formaldehyde using PTR-MS and a Hantzsch monitor. The HCHO mixing ratio was calculated from the m/z 31 signal according to equation 2.2 (reaction rate constant for formaldehyde protonation = $2 \times 10^{-9}$ cm$^3$ s$^{-1}$).

Figure 2.8. During days with low photochemical activity, low solar radiation (August 31 – September 1), and low formaldehyde mixing ratios, the PTR-MS shows higher values than the Hantzsch monitor. During sunny days, the Hantzsch monitor (August 26 – August 29) shows usually higher values, even during the night, when the mixing ratios are similar to the mixing ratios at low photochemical activity. But in contrast to the laboratory comparison, the PTR-MS always measures more than 50% of the Hantzsch monitor. It is interesting to note that on the afternoon of August 27, the PTR-MS shows even significantly higher values than the fluorescent method. This happened in combination with an air mass exchange with advection of dry and clean air (so called foehn event) that caused a general decrease of nearly all pollutants and the relative humidity at the station. The Hantzsch monitor also shows this decrease whereas the PTR-MS produced a similar diurnal cycle as on the day before. A humidity dependence can be excluded, because the moisture remained small for the next two days after dropping on the 27th, and the Hantzsch instrument again shows higher values on the 28th and 29th. On the 29th, the highest HCHO mixing ratios of the whole period were measured by the Hantzsch method, whereas the PTR-MS concentrations were considerably lower than during the days before. This discrepancy cannot be related to meteorological conditions like relative humidity, temperature and radiation. Several publications already show the feasibility of measuring formaldehyde by the fluorometric method used in this work (Slemr et al., 1996; Cárdenas et al., 2000). Assuming that the formalde-
Figure 2.8: Formaldehyde mixing ratios measured by PTR-MS and a Hantzsch monitor for a 7-day-period during the CHAPOP field campaign in southern Switzerland. The HCHO mixing ratio is calculated from the m/z 31 signal according to equation 2.2 (reaction rate constant for formaldehyde protonation = $2 \times 10^{-9}$ cm$^3$ s$^{-1}$).

Most probably other compounds or fragments of other compounds have contributed to the m/z 31 signal. A possible candidate could be methyl hydroperoxide (CH$_3$OOH), as one of its fragments contributes to the m/z 31 signal (A. Hansel, personal communication). Staffelbach et al. (1997) measured methyl hydroperoxide concentrations in southern Switzerland during summer 1994. They found mean mixing ratios (± standard deviation) for a two day period of 0.6 (± 0.23) ppb. Therefore, even if 100% of methyl hydroperoxide are fragmenting to m/z 31 and assuming the calibrated sensitivity of 21%, it is hardly possible to explain the high m/z 31 signal just by fragmentation of CH$_3$OOH. Nitric oxide (molecular weight 30 amu) does not play a role because of a too low proton affinity. But NO$^+$ is produced at large quantities in the hollow cathode. The ionization energy of NO is so low that almost no charge transfer between NO and other compounds takes place after generating NO$^+$ in the ion source. Due to an isotope ratio $^{15}$N/$^{14}$N of 0.37%, $^{15}$NO$^+$ can contribute to m/z 31 in a significant amount (about 1 ppb). This can be considered by subtracting 0.37% of the m/z 30 signal. But no distinct reason for the different HCHO$_{Hantzsch}$/HCHO$_{PTRMS}$ ratios during the field campaign could be identified.
2.3.5 Instrument intercomparison

An intercomparison between the two PTR-MS systems was performed in the laboratory of the Paul Scherrer Institute in October 2002. Ambient air was sampled for one night just outside the laboratory in a rural environment. A calibration was performed before and after the intercomparison with a gas standard containing alkanes, alkenes, alkynes, dialkenes, and aromatics ≤ C₉ at concentrations of a few ppb (National Physical Laboratory, Teddington, UK). Mixing ratios were calculated based on these calibrations.

Figure 2.9 shows the results for m/z 107 (protonated C₂-benzenes) and m/z 43 (protonated propene). The time series of m/z 107 shows elevated mixing ratios in late afternoon and early morning as a consequence of increased traffic when people leave and arrive at the institute. Main sources of C₂-benzenes like xylenes and ethyl benzene are the evaporation of solvents and the evaporation and combustion of gasoline and to a lesser extent diesel (Heeb et al., 2000). Both mass spectrometers closely reproduce all the different features. A significant correlation (R² = 0.84) and a slope of 1.14 with slightly higher values measured by the PTR-MS (FAL) is obtained (small panel in Figure 2.9a). Similar results with close correlations and slopes of 1 ± 0.2 are also obtained for e.g. m/z 57 (butene, butanol), m/z 93 (toluene), and m/z 121 (trimethylbenzene). Within the uncertainty of the measurements, the agreement between the two different instruments is satisfactory. Figure 2.9b shows the time series and the scatter plot for m/z 43 which corresponds to protonated propene. It is emitted even in higher amounts by the traffic than the C₂-benzenes (Staehelin et al., 1998). Propene shows also the highest mixing ratios in the late afternoon and an increase in the morning. There is a discrepancy between the PSI- and the FAL-instrument almost during the whole night, before they compare well in the morning. However, the scatter plot of the PTR-MS (FAL) data vs. the PTR-MS (PSI) data shows a close correlation (R² = 0.93) and a slope of just 0.73 for the whole dataset. Fragmentation of propene or other compounds on this mass might explain this discrepancy. The settings of the two instruments differed slightly (PSI-instrument: pdrift = 2.04 mbar, Udrift = 580 V, Tdrift = 50 °C, E/N = 137.1 Td; FAL-instrument: pdrift = 2.04 mbar, Tdrift ≈ Tair = 23 °C, Udrift = 600 V, E/N = 126.8 Td), which could cause different fragmentation patterns. Warneke et al. (2003) investigated the fragmentation patterns of 75 different VOCs with the PTR-MS using a gas-chromatographic preseparation method and reported major fragments appearing at m/z 43 for 3-methyl-1-butene, 2-methyl-1-butene, 2-methyl-2-butene, trans-2-pentene, 1-pentene, and acetone. Other possible species yielding a fragment of mass 43 are acetaldehyde, butanal, acetic acid and propanol. Tests with the PSI-instrument showed that propene fragments to 40% to mass 41, a mass 43 fragment yield of only 0.4% for acetaldehyde, and 5% for butanal.
Figure 2.9: Intercomparison of two PTR-MS systems. The data represent 15 min averages. One cycle took around 140 seconds, the dwell time for each mass during one cycle was 5 seconds. a) time series and scatter plot for m/z 107 (protonated C₂-benzenes). b) time series and scatter plot for m/z 43 (protonated propene).

2.3.6 Measurements of aromatics, PTR-MS comparison with GC

Figure 2.10 shows the sum of xylenes measured by the GC and of m/z 107 measured by the FAL-instrument during the campaign in Berne in March 2001. Mass 107
2.3. Results and discussion

is attributed to C_2-benzenes (xylenes + ethyl benzene) and benzaldehyde. Benzaldehyde can be produced by the oxidative degradation of toluene (SEINFELD & PANDIS, 1998). Because of low temperatures and frequent rain during this period, we expect only a small contribution from this mechanism. Toluene and the C_2-benzenes as measured at this station are mostly emitted by the traffic. The emission factor of ethyl benzene from traffic is about one magnitude smaller than the emission factor of m-, p-xylene (STAHELIN ET AL., 1998). Therefore, the non-consideration of ethyl benzene by the GC does not change the results significantly. For the calculations of the concentrations (equation 2.2), a weighted mean of the proton transfer reaction rate constants (2.26×10^{-9} \text{ cm}^3 \text{ s}^{-1}) for the xylenes and ethyl benzene was used. The measurements with the two methods agree well regarding the diurnal pattern. The scatter plot of the PTR-MS signal versus the GC signal shows a high correlation (R^2 = 0.91). On average, 78% of the concentration quantified by the GC is found by the PTR-MS as denoted by the slope of the regression line. The correlation (not shown here) between m/z 93 (protonated toluene; measured by PTR-MS) and toluene (measured by GC) shows a slope of 0.86 (R^2 = 0.89). Losses in the instrument itself can probably cause the slightly lower concentrations measured by PTR-MS because the ambient air still passed a mass flow controller before the drift tube at the time of these measurements. As mentioned above, the theoretically calculated reaction rate constants might show

![Graph showing mixing ratios](image)

**Figure 2.10:** Mixing ratios of the sum of xylenes (measured by the GC) and of m/z 107 (C_2-benzenes; measured by PTR-MS) for a 5-day period in Berne, Switzerland in March 2001. Small panel: scatter plot of GC signal versus PTR-MS signal (R^2 = 0.91). Mixing ratios measured by PTR-MS were calculated according to equation 2.2.
an uncertainty of ± 20% (HANSEL ET AL., 1995, 1999). Within these and the uncertainties of the GC measurements (uncertainty < ± 25% (PRÉVÔT ET AL., 2000)), no systematic discrepancy seems to exist and the agreement between the two techniques can be regarded as satisfactory. The reliability of the measurements is also corroborated considering the toluene (m/z 93) to benzene (m/z 79) ratio of 2.2 which is a typical value for fresh traffic emissions (STAEHELIN ET AL., 1998).

During the CHAPOP campaign, clear sky and temperatures up to 27 °C were characteristic for the intensive operation period from August 26 to 29. Afterwards, the meteorological situation changed to lower temperatures and overcast conditions. Figure 2.11 shows some aromatic compounds measured by PTR-MS and GC. There is a big discrepancy between the m/z 107 signal and the C2-benzene mixing ratios of the GC. Moreover, the m/z 107 signal is significantly higher than the m/z 93 and m/z 79 signals. This is most pronounced during the period of high photochemical activity and becomes less distinct at the end of the presented period. Benzaldehyde, which is most of all produced by the toluene degradation contributes to the m/z 107 signal of the mass spectrometer. Estimates taking into account typical emission factors, OH reactivities of the aromatics and a benzaldehyde yield of 6% out of the toluene oxidation (KLOTZ ET AL., 1998) cannot reproduce the measured concentrations. Because of a good correlation of the signal attributed to benzaldehyde with the indoor temperature, we initially presumed a

Figure 2.11: Mixing ratios of benzene (m/z 79), toluene (m/z 93), C2-benzenes + benzaldehyde (m/z 107) (measured by PTR-MS), and the C2-benzenes (xylenes + ethyl benzene) (measured by GC) for a 7-day-period during the CHAPOP field campaign in southern Switzerland. Mixing ratios measured by PTR-MS were calculated according to equation 2.2.
2.3. Results and discussion

contamination due to a possible leakage and some outgassing in the container. But the sudden decline of m/z 107 at around noon of the 27th (due to the foehn event mentioned in Section 2.3.4) and the correlation of this signal with other VOCs like

![Graphs showing scatter plots of C2-benzenes vs. m/z 93 and m/z 107 vs. m/z 93.](image)

Figure 2.12: a) Scatter plot of C2-benzenes (measured by GC) vs. m/z 93 (attributed to toluene; measured by PTR-MS). b) Scatter plot of m/z 107 (attributed to C2-benzenes + benzaldehyde) vs. m/z 93 (both measured by PTR-MS). Mixing ratios measured by PTR-MS were calculated according to equation 2.2. Measurements were performed during the CHAPOP field campaign in southern Switzerland.
benzene do not support this hypothesis. Unexplained contributions to m/z 107 contradict the data of de Gouw et al. (2003) and Warneke et al. (2003), who performed GC-PTR-MS measurements at urban and remote stations. Both publications reported no interfering signals at m/z 107. As our sampling site is surrounded by grassland and trees, the air is burdened by VOCs of biogenic and anthropogenic origin. There are no VOCs of biogenic origin with m/z 107 reported in the literature. It is also difficult to imagine such considerable amounts of other anthropogenically emitted compounds with that mass in the atmospheric boundary layer. However, a contribution of a directly emitted or photochemically oxidized biogenic VOC cannot be excluded. There seems to be a correlation between m/z 107 and the photochemical activity of the air mass as presented in the following. A possible correlation is also corroborated by reaction chamber studies of the photooxidation of α-pinene at the Paul Scherrer Institute (unpublished results). They showed a clearly visible signal on m/z 107 one to four hours after the start of the pinene degradation.

Figure 2.12 shows a scatter plot of the C₂-benzenes mixing ratio (GC) vs. the m/z 93 (attributed to toluene) mixing ratio (panel a) and a scatter plot of m/z 107 (C₂-benzenes + benzaldehyde) vs. m/z 93 (panel b). In Figure 2.12b the data are separated in four time periods with different meteorological conditions. It is obvious that the linear regression slopes decreased within the whole period presented here. For August 26 – 27, the slope reaches nearly 3 (not shown in Figure 2.12b). Later the slope ranges around 1 (August 30 – 31) in agreement with the data in panel a) and becomes even smaller at the end of the measurements. The degree of photochemical processing definitely influences the amount of benzaldehyde in the atmosphere and influences therefore the m/z 107 signal of the mass spectrometer, too. The m/z 107 to m/z 93 data recorded from September 1 to 4 show the best correlation. This can be ascribed to identical sources and no significant (photochemical) conversion of the contributing species to m/z 107 and m/z 93. The fact that this slope is lower than the slope of panel a might indicate a slight under-prediction of the PTR-MS measurements.

2.4 Conclusions

Extensive laboratory and field measurements have revealed important characteristics concerning the performance of the two different versions of the PTR-MS instrument. The features investigated include the background signal stability, the transmission efficiency, the humidity dependence, a comparison with a formaldehyde monitor, an instrument intercomparison, and a comparison with a gas chromatograph.

The newer instrument (PSI) with a temperature stabilization of the inlet system and the drift tube as well as Teflon gaskets instead of Viton performed considerably
2.4. Conclusions

better with respect to signal stability. The background variability as well as the general background level was diminished significantly in the newer version. The maximum daily variation has diminished from 0.27 ppb, 0.51 ppb, and 0.25 ppb to 0.04 ppb, 0.07 ppb, and 0.03 ppb for m/z 79, m/z 107, and m/z 121, respectively. The average blank values decreased from 0.36 ppb, 0.25 ppb, and 0.13 ppb to 0.04 ppb, 0.05 ppb, and 0.05 ppb for m/z 79, m/z 107, and m/z 121, respectively. But even with Teflon seals, frequent background measurements are still recommended to be able to consider potential memory effects or influences of other environmental parameters. During our field campaign background measurements were performed for 30 minutes every 3 hours.

A reliable knowledge of the mass discrimination of the PTR-MS is essential to calculate the mixing ratios of VOCs following the PTR-MS theory. The method proposed in this work with injecting small volumes of liquid compounds into pillow bags seems to be a feasible way to determine the function. The measurements are quickly reaching stable conditions, but are not perfectly reproducible so that the data is characterized by a large scatter. Even if this variability is considered, the curve determined here does not coincide with the curve given by the manufacturer. The transmission determination by the manufacturer might have been at different instrumental settings as those used by us. As a consequence, a determination by the user is highly recommended. A wrong transmission function might be responsible for errors of around 25%.

In contrast to the humidity sensitivity for benzene measurements reported by Warneke et al. (2001) at a drift tube pressure of 2.5 mbar, we found a much less distinct effect. The effect was largest when changing from absolutely dry to slightly humid conditions. Therefore, the effect has to be taken into account in the case of dry calibration conditions. A comparison of the measured and the modeled primary ion cluster distribution showed the inability of the model to reproduce the measurements. An over-proportional increase of the dimer/monomer ratio with humidity may even point to a cluster producing process like a dimer generation in the jet entering the quadrupole.

As already reported in the literature (Hansel et al., 1997; Holzinger et al., 1999), the measurement of formaldehyde with the PTR-MS is problematic due to the low proton affinity of this molecule. The comparison of the PTR-MS with a formaldehyde monitor showed for a dry gaseous HCHO mixture a significant correlation and a sensitivity of 21%. A comparison with laboratory air and during a field campaign showed a significantly larger sensitivity of m/z 31 of the PTR-MS compared with the formaldehyde monitor. This can probably be attributed to an interference due to isobaric compounds or fragments.

The intercomparison between two different PTR-MSs presented satisfactory results for several different masses but pointed again to one of the general problems of PTR-MS measurements. Even if a reliable calibration source is available, a contribution of isobaric molecules can never be excluded because of the mass and
not species-specific sensitivity of the PTR-MS. This comparison has shown furthermore, that the particular settings of the instrument might change the response of the system to changing environmental conditions. Therefore, a detailed characterization of the instrument for these particular settings is strongly recommended.

Atmospheric measurements in cases of low photooxidation conditions showed a good agreement between gas chromatography and proton transfer reaction mass spectrometry for aromatics. Under conditions of high insolation, biogenic as well as anthropogenic VOC sources and photochemically processed air, a substantial discrepancy between the m/z 107 concentration of the PTR-MS and the C₂-benzene concentration of the GC appeared. Known yields of benzaldehyde from the toluene oxidation could not reproduce the differences. Therefore, an unknown compound can significantly contribute to m/z 107 under certain conditions.

As seen in this work, unknown contributors to a certain mass and the fragmentation which is sensitive to the instrument specific settings can complicate the interpretation of the mass spectra considerably. Parallel measurements with another technique (e.g. gas chromatography) therefore ideally complete PTR-MS studies even if they only provide data at lower time resolutions.

Acknowledgements

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Chapter 3

Reaction Chamber Studies of the 1,3,5-Trimethylbenzene/NO\textsubscript{x} Photooxidation

3.1 Introduction

Reaction chambers are a common tool to study the atmospheric photochemistry under controlled conditions. A multitude of publications related to reaction chamber measurements appeared dealing with kinetic studies and photooxidation product distributions (e.g. Klotz et al., 1998; Siese et al., 2001; Volkamer et al., 2001, 2002) as well as with the formation of secondary organic aerosols (e.g. Wang et al., 1992; Forstner et al., 1997; Hoffmann et al., 1997; Kalberer et al., 2000; Jang & Kamens, 2001; Inuma et al., 2004). However, unrealistically high concentrations and 'chamber effects' like adsorption, desorption, decomposition, and possible surface reactions of reactants and products on the wall can lead to artificial results. As these wall reactions should be minimized and especially aerosols suspended in air are subject to deposition losses to the walls of the reaction chambers, it is aimed at having facilities with a high volume to surface ratio. The newly built reaction chamber at the PSI with dimensions of 3x3x3 m\textsuperscript{3} = 27 m\textsuperscript{3} is in this respect an excellent facility allowing to perform experiments at concentration levels low enough so that potential artifacts are minimized.

3.2 Experimental

3.2.1 Chamber description and experimental procedure

The reaction chamber consists of a 27 m\textsuperscript{3} transparent Teflon\textsuperscript{®} bag mounted in a temperature controlled housing with reflecting walls. Four 4 kW xenon-arc lamps
are used as the light source equipped with borosilicate glasses to filter the excessive UV radiation and to mimic natural sunlight conditions. Prior to every experiment, the chamber was flushed with purified air (AADCO 737, pure air generator) for at least 24 hours. After purification, the air was humidified to a relative humidity of 60% by flushing steamed water into the chamber. NO, NO$_2$, and propene were flushed into the chamber using gas bottles of 1000 ppm. The organic reactant (during the experiments presented here only 1,3,5-trimethylbenzene (TMB)) was added by injecting a defined amount of liquid TMB (GC quality, > 99.0%, Fluka) into a heated glass vial that was continuously flushed with pure air. Experiments were performed with initial TMB, NO, and NO$_2$ mixing ratios between 660 and 20 ppb, 160 and 5 ppb, 160 and 5 ppb, respectively. The initial propene mixing ratio was kept constant at 300 ppb. After all gases were added, 30-45 minutes were used to let the gases diffuse and mix homogeneously before turning on the lights. After the experiment, the bag was flushed with purified air and approximately 5 ppm of O$_3$ to clean the chamber and to oxidize the remaining organics.

### 3.2.2 Instrumentation

The parent hydrocarbon (TMB) was monitored with GC-FID (Varian 3400) and PTR-MS whereas the oxygenated oxidation products were measured on-line with the PTR-MS, quasi-on-line with ion chromatography (IC) after sample collection in a wet effluent denuder, and off-line with gas chromatography-mass spectrometry (GC-MS) after sample collection on polyurethane foams. Ozone was measured by UV-absorption (Environics S300), CO with vacuum fluorescence (AeroLaser AL 5002), and NO and NO$_2$ via gas-phase chemiluminescence detection (Monitor Labs 9841A). Prior to detection, NO$_2$ was converted to NO using a molybdenum converter. As this conversion is not only sensitive to NO$_2$ but also to other reactive nitrogen species such as peroxyacetyl nitrates (PAN), the NO$_2$ measurements with this kind of converter show reasonable results in urban areas when interference of PAN and other species is relatively small. In rural and remote locations, as well as in substantially aged air masses (as it is the case in our reaction chamber experiments after several hours), the measurements are ill-defined being sometimes called NO$_x$ what and are only of minor information. A photolytic converter that shows usually negligible interferences of other nitrogen species was purchased. Due to quite unstable conversion efficiencies, no reliable NO$_2$ measurements were available.

Aerosol related measurements were performed with two condensation particle counters (CPC) measuring the total particle number concentration (TSI 3022 and 3025A), with a scanning mobility particle sizer along with a CPC measuring the particle size distributions (Wang & Flagan, 1990), and with a volatility tandem differential mobility analyzer measuring the volatile fraction of size selected aerosols (Rader & McMurry, 1986). Chemical analysis of the particles were conducted quasi-on-line with IC, and off-line by GC-MS, infrared spectroscopy, and laser des-
3.3 Master Chemical Mechanism

The gas phase chemistry was modeled with the Master Chemical Mechanism (MCM), version 3 (Jenkin et al., 1997, 2003; Saunders et al., 2003, http://chmlin9.leeds.ac.uk/MCMframe.html). FACSIMILE, a software for modeling processes and chemical reactions was used to solve the differential equations. The freely available mechanism includes kinetic and mechanistic data to the tropospheric degradation of VOCs and the production of secondary pollutants. No heterogeneous processes and no particle phase are included. The near-explicit mechanism contains in total 12,691 organic reactions, 46 inorganic reactions, and 4,351 species. Not all of the reactions are explicitly studied. Therefore the mechanism is based on the assumption that the kinetics and the products of the unstudied reactions can be defined on the basis of the known reactions of a comparatively small number of similar chemical species by analogy and with the use of structure-reactivity correlations. In our work that focused on the TMB degradation under the presence of propene, a reduced mechanism with 616 reactions and approximately

![Figure 3.1: Schematic of the OH-degradation of 1,3,5-trimethylbenzene as represented in the Master Chemical Mechanism, v3. Main products are labeled with their names, other species are labeled with their MCM code. Encircled species are discussed in section 3.5.](image-url)
200 species was used. Figure 3.1 illustrates the first steps of the TMB degradation chemistry initiated by the reaction with OH radicals according to the MCM.

Due to a large number of laboratory studies on the atmospheric oxidation of aromatic hydrocarbons in the last years (Calvert et al., 2002), considerable improvement in the understanding of the detailed chemistry has been achieved. However, publications related to the photooxidation of 1,3,5-TMB are limited (Yu et al., 1997; Smith et al., 1999; Kleindienst et al., 1999; Cocker et al., 2001) and ring-opening routes are still speculative whereas ring-retaining routes are comparatively well understood (Hamilton et al., 2003). Until now, only two studies are published that address a MCM comparison with reaction chamber data for aromatic hydrocarbons. Wagner et al. (2003) used a reaction chamber experiment at EUPHORE (Valencia, Spain) to validate the toluene degradation sub-mechanism. Hamilton et al. (2003) analyzed four experiments at the same facility to compare the 1,3,5-TMB mechanism with experimental data. They used a GCxGC technique and identified only three oxidation products in their chromatograms.

### 3.4 Chemical reactions leading to radicals

TMB does not dissociate by solar radiation, and the reaction of TMB with O(3P) is unimportant in the troposphere (Calvert et al., 2002). The reaction of TMB with O₃ is too slow to be considered in the chemical mechanism. Therefore, the TMB degradation is only initiated by reaction with OH- and NO₃-radicals. Table 3.1 shows the reaction rate constants for the reactions of TMB and propene with O₃, NO₃ and OH. Since the concentrations of the reaction partners are substantially different in our reaction chamber system, it is important to take their levels into account to ascertain the main reaction pathways. As already mentioned in Chapter 1, O₃ is produced by reactions 1.2 and 1.1. OH radicals are either formed via the photolysis of O₃ (reactions 1.7 and 1.8) or through the photolysis of formaldehyde (\(\lambda \leq 360\) nm)

\[
HCHO + h\nu \rightarrow H^+ + HCO^-
\]  \hspace{1cm} (3.1)

followed by

\[
H^+ + O_2 + M \rightarrow HO_2 + M
\]  \hspace{1cm} (3.2)

\[
HCO^- + O_2 \rightarrow HO_2 + CO
\]  \hspace{1cm} (3.3)

\[
HO_2 + NO \rightarrow OH^- + NO_2
\]  \hspace{1cm} (3.4)

and in analogy through the photolysis of higher aldehydes (e.g. acetaldehyde (\(\lambda < 345\) nm))
3.4. Chemical reactions leading to radicals

\[ CH_3CHO + h\nu \rightarrow CH_3 + HCO \]  
(3.5)

Further OH radical sources are the ozonolysis of alkenes (Paulsen & Orlando, 1996) and the photolysis of nitrous acid (HONO) (\( \lambda \leq 390 \text{ nm} \))

\[ HONO + h\nu \rightarrow OH^- + NO \]  
(3.6)

HONO is formed via the recombination of OH radicals with NO

\[ NO + OH^- + M \rightarrow HONO + M \]  
(3.7)

leading to no new radical species, but also via the surface-catalyzed reactions (Finlayson-Pitts & Pitts Jr., 2000)

\[ NO + NO_2 + H_2O \rightarrow 2HONO \]  
(3.8)

\[ 2NO_2 + H_2O \rightarrow HONO + HNO_3 \]  
(3.9)

As the MCM is only restricted to homogeneous processes, the last two reactions are not included in the model. These reactions can probably influence the radical conditions considerably in the reaction chamber, because particles and most of all the chamber walls can provide the surfaces. Subsequently, HONO can be probably generated in significant amounts in the reaction chamber, especially between injection of the reactants and the beginning of the irradiation (Sakamaki & Akimoto, 1988). Investigations of the HONO formation at the EUPHORE chamber showed that the initial HONO formation depended on the history of the chamber and the NO\(_x\) loading (Wagner et al., 2003).

The NO\(_3\) radical is produced via reaction 1.9 and to a small amount via the reaction of atomic oxygen with NO\(_2\).

\[ O + NO_2 + M \rightarrow NO_3 + M \]  
(3.10)

Figure 3.2 presents the modeled time series for O\(_3\), NO\(_3\), and OH during the first 60 min of a typical experiment with starting conditions of 585 ppb TMB, 300 ppb Table 3.1: Rate constants for TMB and propene. \( k \) in cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), \( k' \) in s\(^{-1}\). \( k' \) denotes the pseudo-first order rate constants after 30 min of a typical reaction chamber experiment.

<table>
<thead>
<tr>
<th>compound</th>
<th>( k )</th>
<th>( k' )</th>
<th>( k )</th>
<th>( k' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMB</td>
<td>slow</td>
<td>8.8E-16</td>
<td>slow</td>
<td>5.7E-11</td>
</tr>
<tr>
<td>C(_3)H(_6)</td>
<td>9.1E-18</td>
<td>3.1E-10</td>
<td>9.4E-15</td>
<td>1.7E-5</td>
</tr>
<tr>
<td>C(_3)H(_6)</td>
<td>2.3E-6</td>
<td>3.3E-9</td>
<td>2.9E-11</td>
<td>8.8E-6</td>
</tr>
</tbody>
</table>
propene, 133 ppb NO₂, and 137 ppb NO. Initially, all three species regarded were assumed to be zero. The O₃ concentrations after 60 min are approximately 5 orders of magnitude bigger than the concentrations of the two radicals. The O₃ mixing ratio jumps already after one minute to a value of 7 ppb and reaches 10 and 33 ppb after 30 and 60 min, respectively, whereas NO₃ and OH do not exceed 0.15 and 0.05 ppt within the first hour. Table 3.1 lists the pseudo-first order rate constants after 30 min based on the calculations presented in Figure 3.2. The Table shows that the main initial step of the atmospheric oxidation of TMB in the reaction chamber is the reaction with OH (as also expected for ambient air conditions).

For propene, the reactions with O₃ and OH are nearly equal whereas the reaction with NO₃ can be disregarded during the beginning of the experiment. The addition of propene in reaction chamber experiment is a common procedure to generate a sufficient level of OH radicals to initiate the degradation processes (Odum et al., 1996). The molar yields from the propene + OH reaction are 0.86 and 0.98 for formaldehyde and acetaldehyde, respectively (Seinfeld & Pandis, 1998). The gas-phase reaction of propene + O₃ results in a formation yield of approximately 0.7 and 0.5 for formaldehyde and acetaldehyde (Calvert et al., 2000). As already described above, the aldehydes will photolyze in the reaction chamber and act therefore as an OH radical precursor. Due to the high aldehyde yields of the propene degradation, the addition of propene results in a faster inception of the experiments.
3.5 Results

More than 25 experiments studying the 1,3,5-trimethylbenzene/propene/NO\textsubscript{x} photooxidation were conducted in the year 2003 upon completion of the reaction chamber. Most of the experiments were performed with initial TMB mixing ratios of around 600 ppb and 320 ppb NO\textsubscript{x}. This input concentration ensured a large enough secondary aerosol mass that could be physically and chemically analyzed by the above mentioned measurement techniques (see Section 3.2.2). Lower concentrations could result in too long sampling intervals and too large sampling volumes for the aerosol analysis. Extensive sampling for the various measurements could subsequently led to a collapse of the Teflon bag and a non-ideal volume to surface ratio. In the other experiments the TMB and the NO\textsubscript{x} concentrations were always kept at the same relative amount. Figure 3.3 shows the maximum O\textsubscript{3} mixing ratios for a number of MCM simulations. The straight line illustrates the range of the experimental starting conditions. All experiments were conducted under NO\textsubscript{x} limited O\textsubscript{3} formation conditions, that means a change of the VOC input would not change the O\textsubscript{3} maxima whereas the maxima are sensitive to the NO\textsubscript{x} input.

The results of a model-experiment comparison are shown in Figure 3.4 and Figure 3.5. The starting conditions were 585 ppb TMB, 300 ppb propene, 133 ppb NO\textsubscript{2}, and 137 ppb NO. Besides the reactant, selected oxidation products are illustrated as well. Methylglyoxal (measured with PTR-MS as m/z 73) is the main oxidation product. Dimethylfuranone and methyl-oxo-pentenal are produced via

\begin{figure}[h]
  \centering
  \includegraphics[width=0.5\textwidth]{figure3.3.png}
  \caption{Simulated maximum O\textsubscript{3} mixing ratios for different initial reactant mixing ratios. Contour lines are based on 18 model runs. Numbers in squares denote the results of the simulations. The straight line illustrates the range of starting conditions.}
\end{figure}
the same reaction pathways (see Figure 3.1). Since both compounds have the same mass, they cannot be distinguished by the PTR-MS, in the same manner as methylfurandione that is a subsequent product of the 2-methyl-4-oxo-2-pentenal with NO₃ reaction (all three species measured at m/z 113). All three compounds are also added in the MCM output for comparison with the experiments. Dimethylbenzaldehyde (measured as m/z 135) is only produced via a minor reaction pathway. The formation of pyruvic acid is not illustrated in Figure 3.1. This species is produced through the reaction of 'TM135OXMC' (see Figure 3.1) with O₃ and subsequent reactions. Pyruvic acid is included in the model-experiment comparison as it can play an important role in the formation of secondary organic aerosols (SOA). The modeled and measured progression of TMB and the selected oxidation products show a qualitative agreement taking into account the experimental errors and the uncertainties of the model. Besides the already mentioned chamber effects,
the main experimental errors are the identification of the products as well as the possible fragmentation of larger molecules. Furthermore, no calibrations standards were available for these oxidation products. Therefore, we used an 8-component standard including TMB, propene, toluene, and oxygenated VOCs (Apel & Riemer Environmental Inc., Denver, USA) to determine the sensitivity of the instrument and calculated the mixing ratios of the oxidation products using computed reaction rate constants (for details see Chapter 2) and corrected the results according to the calibrated sensitivity. The model results can be biased due to unconsidered reactions, erroneous reaction rate constants, wrongly assumed light conditions and photolysis rates, and missing heterogeneous reactions at the wall and on aerosol surfaces. With progression of the experiment, a good model-experiment agreement is less likely as more and more processes are involved and the effects of deviations in the kinetics between the model and the experiment are exponentiated. Considering all these facts, the TMB degradation and the time series of the main organic products seem to agree acceptably. Especially the oxidation products with small formation yields like dimethylbenzaldehyde and pyruvic acid seem to be nicely reproduced, in contrast to a recent publication of Hamilton et al. (2003) that suspects a lower yield for the dimethylbenzaldehyde pathway as it is included in the MCM. But their measurements were all distinctly below the simulations and the observed relative concentrations are also not reproduced by the model.

A closer look reveals some severe discrepancies. The methylglyoxal maximum is 1.5 times higher in the model, and the measured sum at m/z 113 stays at around 5 ppb during the second half of the presented period whereas the modeled sum of the contributing compounds converges to nearly zero again. The exact shape of the TMB decay is different for the simulation and the measurements, and the measured TMB steadily decreases whereas only a slight TMB decrease is simulated by the MCM after 240 min (see Figure 3.6). The comparison for the inorganic species does not show a satisfactory agreement. The simulated NO decay is about 60% slower than the measured one. The CO formation is quantitatively reproduced during the first 1.5 hours but is finally approximately 100% over-predicted by the MCM after 480 min. The predicted O₃ maximum after around 180 min is nearly the double of the measured concentration. Figure 3.6 shows a direct model-experiment comparison for TMB, O₃, NO, and OH radicals. The experimental OH radicals are derived from the measured TMB decay (assuming OH as the only TMB sink and a known TMB + OH rate constant) after applying a low-pass filter to the TMB data. The discrepancies of the OH curves in the beginning could be partly related to the (low-pass) filtering process of the TMB data as the fitting function is less stable at the edges of the data series. The time of the OH maximum is nearly identical but the modeled OH level drops to 2.5 x 10⁵ molecules cm⁻³ at 200 min and stays nearly constant for the rest of the model simulation. The bend after 200 min appears due to a strongly declining
Figure 3.6: Experimental (thin lines) and simulated (thick lines) data for TMB, \(O_3\), NO, and OH radicals. 'Experimental' OH radicals are derived from the decay of TMB after applying a low-pass filter.

OH source via the reaction of \(HO_2\) with NO. The 'measured' OH concentrations also decrease after 120 min but remain at around \(8.5 \times 10^5\) molecules cm\(^{-3}\). These differences in the OH profiles can explain the different shapes of the TMB curves: a faster measured TMB decay in the beginning, probably due to more OH from the HONO photolysis, a more rapid simulated TMB decay after 75 to 130 min, and subsequently a stronger measured TMB decay due to an under-prediction of the OH levels by the model. The over-prediction of \(O_3\) by the model can be partly explained by the over-predicted OH formation by the model. The modeled \(O_3\) is rising strongest between 80 and 150 min when the modeled OH exceeds the measured OH most. This is also in line with the over-predicted methylglyoxal, the main oxidation product of TMB, by the model. As the NO decline is slower in the model, the simulated radical turnover from \(HO_2\) to OH (via the reaction with NO) is higher, generating high OH concentrations. A reason for the too fast NO decrease during the experiment could be an underrated formation of (thermally instable) nitrates in the model as experiments provide an indication of a substantially thermally unstable signal at m/z 46. m/z 46 can be at least partly attributed to \(NO_2^+\) that is produced via the reaction of \(H_3O^+\) with PAN (HANSEL & WISTHALER, 2000).

A similar model-experiment conflict for \(O_3\) was already observed by WAGNER ET AL. (2003) who investigated the toluene degradation. But their model run predicted a toluene decay that was 28% too slow compared to the experiment, corresponding to an under-prediction of the oxidation capacity. Consequently, they addressed the divergency to a missing OH source that is not coupled with
3.5. Results

A conversion of NO to NO₂ like the ozonolysis of alkenes or the isomerization of peroxo-radicals. Another reason mentioned could be missing NO₃ chemistry that converts reactive nitrogen species into stable species in combination with a ROₓ radical formation.

A crucial process for the amount of OH radicals produced seems to be the split ratio of 'TM135BPRO' into methylglyoxal and methyl-pentenal and methylglyoxal and dimethylfuranone, respectively (see Figure 3.1). The reaction of dimethylfuranone with O₃ is one of the major OH sources in the MCM simulation. A model run with a yield ratio of 0.8 (methyl-pentenal path) to 0.2 (dimethylfuranone path) instead of 0.5 for both paths reduced the OH radical concentration at its maximum for 25%. Until now, the ring-opening routes are not satisfactory investigated so that different rate constants are rather possible. This could be one reason for the discrepancies in the OH concentrations that is important for the time series of most of the species.

Figure 3.7 shows the corresponding model experiment comparison to Figure 3.4, but for an experiment with only \( \frac{1}{10} \) of initial reactants. The starting conditions were 36 ppb TMB, 10.5 ppb NO, and 11.4 ppb NO₂. The propene mixing ratios remained 300 ppb. The comparison confirms the above discussed results. The modeled and measured TMB decays show the same features. The methylglyoxal profiles diverge less when the model reaches the maximum, but the experimental data increase over the whole considered period whereas the MCM predicts a decrease after 180 min. The simulated O₃ maximum (130 ppb) is twice as high as the measured one (not shown here). Figure 3.7 illustrates that experiments with concentrations comparable to ambient air conditions are possible. No generally different features were observed between high and low concentration experiments. The main oxidation products can be still clearly measured with starting conditions of 36 ppb whereas

![Figure 3.7](image-url)

**Figure 3.7:** Experimental (left) and simulated (right) time series of TMB and selected oxidation products for the experiment on June 06, 2003. Please note the multiplication factors for dimethylbenzaldehyde and pyruvic acid. For the assignment of the masses, see Figure 3.4.
oxidation products with low yields like pyruvic acid are close to the detection limit of the PTR-MS, and are therefore subject to a large scatter.

Owing to a lack of appropriate experimental data, quantitative evidence for the intermediates and the main oxidation products of 1,3,5-TMB are scarce. Apart from the recent publications of Hamilton et al. (2003) that only concentrated on three products, no other direct MCM-experiment comparison is available in the literature. A comparison with the other above mentioned TMB degradation studies (Yu et al., 1997; Smith et al., 1999; Kleindienst et al., 1999; Cocker et al., 2001) is not meaningful because the MCM reaction scheme is based on these studies. Thus, our measurements can help to improve the current understanding of the degradation of TMB and can supply reliable data to validate the chemical mechanism. A modification of the MCM based on our results is for the moment beyond the scope of the current analysis, as the main focus of the reaction chamber experiments was the investigation of the SOA formation from gaseous precursors. Therefore, the monitoring of the gas-phase species provided a good basis to understand the processes of the SOA formation. LDI-MS measurements of aerosol collected on steel plates showed that masses up to $m/z$ 900 could be found with increasing intensity with time during $7\frac{1}{2}$ hours after particle nucleation. Mass spectra of synthetic mixtures and volatility measurements of the aerosols confirmed the results. Consequently, it was concluded that polymerization reactions contribute to the SOA formation so that about 50% of the aerosol mass consisted of polymers after 20 hours of illumination (Kalberer et al., 2004). The proposed polymer-

Figure 3.8: Proposed polymerization reactions during the SOA formation (Kalberer et al., 2004). Species shown in Figure 3.4 are encircled.
3.6 Conclusions and Outlook

This study presented reaction chamber experiments to investigate the photo-oxidation and the formation of secondary organic aerosols of a 1,3,5-trimethylbenzene/propene/NO\textsubscript{x} mixture. Experiments with low initial concentrations, nearly representative for ambient air conditions, showed the feasibility of low concentration experiments. Results from the monitoring of gaseous species helped considerably to improve the understanding of the driving processes of the formation of secondary organic aerosols. Model calculations were performed with the Master Chemical Mechanism to simulate the progression of the gaseous reactants and their oxidation products. A model experiment comparison showed that the overall features of the measurements were satisfactorily reproduced (e.g. the main oxidation products were generated in reasonable amounts), but a detailed comparison revealed substantial discrepancies that could be at least partly attributed to differences in the radical budget. The comparison provided first suggestions for the crucial mechanisms that have to be investigated in more detail.

Future sensitivity studies with the MCM should be conducted to ascertain further decisive processes determining the radical budget in the model. More experiments should be performed to get a deeper insight into the dominating processes during the experiments. Different initial conditions should be chosen to investigate the system under different conditions of limitation regarding the O\textsubscript{3} formation. Wagner et al. (2003) mentioned that the toluene reaction system is far more complex and difficult to understand at NO\textsubscript{x}-limited than under VOC-limited conditions. On the other hand, they showed that the O\textsubscript{3} production is most sensitive to changes of the yields of intermediates, photolysis rates, and rate coefficients at low VOC/NO\textsubscript{x} ratios, i.e. VOC-limited conditions. As shown in this Chapter for TMB, a thorough understanding of the TMB photooxidation is a challenging task under NO\textsubscript{x}-limited conditions.

References


References


Chapter 4

Volatile organic compounds in the Po Basin. Part A: anthropogenic VOCs

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Abstract Measurements of volatile organic compounds (VOCs) were performed in the Po Basin, northern Italy in early summer 1998 within the PIPAPO project as well as in summer 2002 and autumn 2003 within the FORMAT project. During the three campaigns, trace gases and meteorological parameters were measured at a semi-rural station, around 35 km north of the city center of Milan. Low toluene and benzene concentrations and lower toluene to benzene ratios on weekends, on Sundays, and in August enabled the identification of a 'weekend' and a 'vacation' effect when anthropogenic emissions were lower due to less traffic and reduced industrial activities, respectively. Recurrent nighttime cyclohexane peaks suggested a periodical short-term release of cyclohexane close to the semi-rural sampling site. A multivariate receptor model analysis resulted in the distinction of different characteristic concentration profiles attributed to natural gas, biogenic impact, vehicle exhaust, industrial activities, and a single cyclohexane source.

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4.1 Introduction

Volatile organic compounds (VOCs) play a central role in the photochemistry of the atmospheric boundary layer. In the presence of sunlight and catalyzed by the oxides of nitrogen (NO$_x$), VOCs lead to the production of ozone (O$_3$) as already shown in the 1950s (Haagen-Smit, 1952). The VOCs present in the boundary layer are of anthropogenic as well as biogenic origin. On a global scale, biogenic emissions dominate, but in non-rural areas anthropogenic activities (particularly traffic and industrial processes) can provide large VOC emission sources that can lead to high hydrocarbon concentrations in the urban boundary layer. Incomplete combustion of fossil fuels releases mostly hydrocarbons (alkanes, alkenes, aromatics), whereas organic solvents and their vapors also contain considerable amounts of oxygenated hydrocarbons (FRIEDRICH & OBERMEIER, 1999). Aromatic compounds are often used as markers to identify the origin of the air masses (WINKLER et al., 2002; CHRISTENSEN ET AL., 1999) and are of particular interest due to their large abundance in motor vehicle emissions, their role in the ozone and aerosol formation (SEinfeld & PANDIS, 1998; KALBERER ET AL., 2004), and their adverse health effects (GUERRA ET AL., 1995) including benzene, which is rated as human carcinogen.

The Milan area, located in the Po Basin is the most industrialized and densely populated region in Northern Italy (NEFTEL ET AL., 2002). Among the large urban areas in Europe, the Greater Milan area and the surrounding Po Basin are known as one of the regions that are most strongly affected by primary (GUERRA ET AL., 1995) and secondary pollutants (PRÉVÔT ET AL., 1997; THIELMANN ET AL., 2001; DOMMEN ET AL., 2002). A high-resolution emission inventory for a weekday in May 1998 for the Po Basin revealed that stationary sources dominate the VOC emissions whereas the traffic emissions contribute half as much and biogenic emissions are only significant during the sunlight hours (DOMMEN ET AL., 2003). Besides the large emissions in this area, typical meteorological conditions characterized by frequent calm winds, thermal inversions, and high-pressure systems also favor the accumulation of atmospheric pollution (BARDESCHI ET AL., 1991).

The presented measurements were part of the two field studies, Pianura Padana Produzione di Ozono (PIPAPO, ozone production in the Po Basin) and Formaldehyde as a Tracer of Oxidation in the Troposphere (FORMAT). The field experiment PIPAPO took place from May 06 to July 14, 1998 as a part of the EUROTRAC-2 subproject Limitation of Oxidation Production (LOOP) (NEFTEL ET AL., 2002). During this period, field measurements were performed at more than 30 ground stations between the city of Milan and the Alps north of Milan as well as on-board of a research aircraft. The project aim was the research on the evaluation of the temporal and spatial extent of the VOC and NO$_x$ sensitivity of the ozone formation. Two of the main measurement sites during the PIPAPO campaign were Bresso and Verzago, both located north of downtown Milan. VOC data were available for 56
4.2 Measurement sites, techniques, and meteorological conditions

4.2.1 Measurement sites

The measurements presented in this work were performed at Verzago, around 35 km north of the city center, and at Bresso, approximately 5 km north of downtown Milan. The measurement site at Verzago was situated in a semi-rural environment. The measurement containers were placed at the border of a corn field outside a small village. Local anthropogenic emissions originated only from a small blind alley passing the measurement containers and a few houses nearby. The nearest major road that connects Como and Bergamo was located one kilometer northeast of the measurement site. The surrounding area was patchy with fields, meadows, forests, and small villages. Thus, the local environment was not homogeneous with respect to biogenic and anthropogenic emissions.

The measurements at Bresso were carried out on a private airfield inside the freeway belt around Milan, within a densely populated suburb of the city with some light industry. Road traffic and two close gas stations were the main local anthropogenic emission sources. Vehicle emissions were present at nearly every time of the day due to heavy traffic on the highway and another main road just 50 m west of the airfield.

In summer, the topography leads to orographically and thermally induced valley winds. Consequently, southerly winds prevail during daytime between Milan and the Alpine foothills. Therefore, Po Basin air is advected towards the Alps, the Milan plume drifts north into the direction of Switzerland and Verzago is often
located downwind of Milan during daytime in summer (Prévôt et al., 1997; Staffelbach et al., 1997; Thielmann et al., 2002).

4.2.2 Trace gas measurements

GC-FID (Airmotec HC1010)

A commercial Airmotec HC1010 gas chromatograph (Konrad & Volz-Thomas, 2000) (ChromatoSud, Saint Antoine, France) was used in 1998 (at Bresso and Verzago) (Grübler, 1999) and 2002 (at Verzago) to measure hydrocarbons between C4 and C10. Sample air is pulled through adsorption tubes containing Carbopack B and Carbosieve III. After thermal desorption, the hydrocarbons are cryo-focused using a fused silica capillary packed with Carbopack B and cooled with CO2. Injection onto the chromatographic column proceeds after fast desorption at 350 °C. The stationary phase of the separation column consists of 2.5% phenyl- and 97.5% methyl polysiloxan (BGB Analytik AG, Anwil, Switzerland). A flame ionization detector (FID) is used for detection and quantification. A measuring cycle consisted of 29 min sampling, 1 min transferring the sample to the capillary column, and 9 min for chromatography. A new sample can be drawn while analyzing the previous sample. Therefore, quasi-continuous measurements with 30 min time resolution were conducted. In 1998, elaborate calibrations and inter-comparisons were conducted before and after the campaign (Grübler, 1999). During the campaign, a benzene standard was used for calibration (Thielmann et al., 2001). In 2002, calibrations were performed in the field with a gas standard containing alkanes, alkenes, alkynes, dialkenes, and aromatics < C9 at concentrations of a few ppb (National Physical Laboratory, Teddington, UK) and a benzene standard of 750 ppb (BOC Gase, Multigas, Bienne, Switzerland).

PTR-MS (Ionicon Analytik)

A proton transfer reaction mass spectrometer (PTR-MS) was used for VOC measurements at Verzago in 2002. The measuring method is based on a proton-transfer reaction of hydronium ions (H3O+) to compounds with a higher proton affinity than water taking place in a drift-tube reactor, and subsequent detection of the product ions in a quadrupole mass spectrometer (Balzers QMG422). Most common volatile organic compounds in the atmosphere, excluding the alkanes and small alkenes/alkynes, exhibit sufficient high proton affinities (NIST, 2003). The proton-transfer takes place at relatively low energies and therefore causes only little fragmentation of most of the ion products. The whole inlet system both outside and inside the instrument was made out of Silcosteel® (Restek, Bellefonte, U.S.A.) tubes. The inlet tubing, as well as the tubing in the instrument and the drift-tube were temperature stabilized to 50 °C to improve the instrument stability and to minimize the variability of the background signal (Steinbacher et al., 2003).
4.2. Measurement sites, techniques, and meteorological conditions

The background signal was measured every 3 hours for 30 min using an activated charcoal cartridge in the sampling line. In the default mode, 30 selected masses were measured, each of them with a dwell time of 10 sec, resulting in a cycle time of 4 1/2 min. Four times a day full scans from 20 amu up to 150 amu (dwell time per mass 2 sec) were conducted. One full scan cycle took around 4 1/2 min. Due to the proton transfer, VOCs are usually identified at their parent mass + 1. Thus, benzene and toluene were measured at m/z 79 and m/z 93, respectively. However, because of the lack of chromatographic separations, isomers cannot be quantified individually. Calibrations were performed with the same standards as used for the Airmotec GC-FID calibration in 2002.

**GC-FID (Varian 3400)**

For the analysis of VOCs between C₂ and C₇ in the FORMAT campaign 2003, a gas chromatograph equipped with a flame ionization detector (GC-FID, Varian 3400) was used. VOCs from 200 ml of air were enriched on a cooled microtrap (-30 °C) by a thermodesorber (Perkin-Elmer, Turbomatrix) at a flow rate of 10 ml/min during 20 min. After trapping, VOCs were introduced directly into the GC by conductive heating of the trap to 250 °C at 40 °C/min. Analysis was performed on an Al₂O₃/KCl PLOT column (50 m x 0.53 mm i.d.) with He as carrier gas. Calibration runs were made every week with a 30-component standard in the ppb range (NPL, Teddington, U.K.).

**Other trace gas and aerosol measurements**

Apart from the organic compounds and meteorological parameters, a wide range of inorganic compounds (carbon monoxide, ozone, nitrogen oxides, other reactive nitrogen, radon) and aerosols were measured during the different campaigns. Species of interest within this work are most of all ozone, nitrogen oxides, and carbon monoxide. Ozone was measured by UV absorption (Environics) and nitrogen oxides by ozone chemiluminescence (Eco Physics, MonitorLabs). In 2002, nitrogen dioxide was measured by luminol chemiluminescence (for details see DOMMEN ET AL. (2002)). CO was measured at Verzago in 1998 with a conventional non-dispersive infrared detector (Horiba), in 2002 and 2003 by UV-vacuum fluorescence (Aero-Laser). Meteorological parameters like temperature, wind speed and direction, humidity, and radiation were measured during the three campaigns.

**4.2.3 Meteorological conditions and ozone concentrations**

A description of the meteorological conditions during the PIPAPO campaign is given by NEFTEL ET AL. (2002). Besides the two intensive observation periods (May 12-13 and June 1 to 10, 1998) with sunny conditions, a third sunny and warm period due to a high pressure system over western Europe occurred from June 16
to June 23. During the last period, maximum temperatures reached up to 30 °C, and ozone levels rose to 145 ppb at Verzago whereas maximum O₃ mixing ratios of up to 150 ppb and 200 ppb were detected at Bresso and Verzago, respectively, during the first intensive period (Spirig et al., 2002; Thielmann et al., 2002).

During FORMAT 2002, three fair weather periods were encountered. The first period appeared from July 22 to July 30, the second from August 6 to 8, and the third from August 12 to 18. Ozone mixing ratios stayed always below 95 ppb, even when afternoon temperatures reached 30 °C, reflecting a generally less polluted boundary layer.

The FORMAT campaign 2003 started with a foehn event on September 12 followed by stable anticyclonic conditions associated with a ridge stretched from Eastern Europe towards North Africa at high and mid levels. Meteorologically stable conditions prevailed until September 22 when a trough passed the Po Basin, which resulted in a drop of the afternoon maximum temperature from 28.2 °C (September 21) to 21.7 °C (September 23). Within the same period, afternoon maximum ozone mixing ratios dropped from 132 ppb to 44 ppb. The highest ozone mixing ratios were observed on September 20 with 138 ppb.

4.3 Results and Discussion

4.3.1 Aromatic compounds

Figure 4.1 and 4.2 show typical time series of aromatic compounds during the campaigns in 1998 and 2003. A distinct toluene peak occurred usually around noon time, also accompanied by elevated C₂-benzene levels (not shown) whereas the benzene concentrations stayed nearly constant. The peaks appeared during south-southwesterly winds with wind speeds between 1.5 and 2.5 m/s in 1998 and between 1 and 2 m/s in 2003. Several reasons point to an industrial release as the origin of these midday peaks. Firstly, we assume that industrial activities take place during the working days but not during weekends. Similar meteorological conditions prevailed on Sunday, June 21, 1998 and Sunday, September 21, 2003 but comparable peaks were not detected. Secondly, the use of benzene as a solvent is forbidden in Italy, which could explain the low benzene levels even when the other aromatics were high. Thirdly, aromatic emissions from traffic usually show a good correlation between benzene and toluene as it is observed for Bresso in 1998 (see Figure 4.3, small panel). Figure 4.3 also shows a characteristic 6-day time series for benzene and toluene at Bresso. Usually, the highest mixing ratios of anthropogenic VOCs were found during the night due to an accumulation of traffic emissions close to the measurement site in the shallow nocturnal boundary layer. An extreme event was observed in the early morning of May 30, 1998. In contrast to Verzago, the benzene mixing ratios are well correlated with the other aromatics even during the day (e.g. see the simultaneous peaks of benzene and toluene on May
4.3. Results and Discussion

Figure 4.1: Time series of wind speed, wind direction, and aromatic compounds at Verzago measured with GC-FID in 1998.

Figure 4.2: Time series of wind speed, wind direction, benzene, and toluene at Verzago measured with GC-FID in 2003.
supporting the hypothesis of traffic emissions as the main source. Nevertheless, it should be mentioned that the toluene to benzene ratio reflected by a slope higher than 4 in Figure 4.3 is twice the ratio of the corresponding emission factors derived from a tunnel study in Switzerland in 1993 (STAEHELIN ET AL., 1998). In Italy, the benzene content in the gasoline was limited by law to 1% already in 1998 (DOMMEN ET AL., 2003; GÜEBLER, 1999), whereas fuel with up to 5% benzene was allowed in Switzerland at the same time. The mean benzene content of the Swiss car fleet constituted 2.3% in 1993 (HEEB ET AL., 2000). In the beginning of 2000, restrictions to 1% benzene content were also implemented in Switzerland resulting in a toluene/benzene increase from 1.7 to 3.4 in Duebendorf, a suburban sampling site close to Zurich, between 1998 to 2001.

Analyzing the benzene to toluene scatterplot for Verzago in 1998 (see Figure 4.4), a lower correlation than in Bresso is recognizable. Due to the longer lifetime of benzene compared to toluene (SEINFELD & PANDIS, 1998), it would be expected to detect lower toluene to benzene ratios if the traffic emissions are farther away from the measurement site due to the ageing of the air mass. However, higher toluene to benzene ratios (slope of 7.7) were found around noontime (11 AM to 2 PM) in line with the interpretation of the advection of industrial emissions at this time. A slope of 4.7 for all other cases is comparable to the ratio at Bresso and to data obtained from the Regione Lombardia (Direzione Generale Qualità dell'Ambiente, http://www.ambiente.regione.lombardia.it/webqa/aria/Archivio.htm) close to
4.3. Results and Discussion

Figure 4.4: Scatterplot of toluene vs. benzene at Verzago in 1998. Panel a) distinction of cases around noontime (11 AM to 2 PM) and other daytimes. The slopes of the orthogonal regression lines are 7.7 and 4.7 for 11 AM to 2 PM data (dashed line, $R^2 = 0.53$) and the rest of the data (solid line, $R^2 = 0.64$), respectively. Panel b) distinction of weekday, Saturday, and Sunday cases. The slopes of the orthogonal regression line are 5.7 (weekday, grey line, $R^2 = 0.59$), 3.8 (Saturday, solid black line, $R^2 = 0.70$), and 3.4 (Sunday, dashed line, $R^2 = 0.85$).
It is obvious that the lowest toluene to benzene ratios and the highest correlation without any enhanced toluene mixing ratios were found on Sundays. A slightly higher slope with a few cases of elevated toluene mixing ratios was measured on Saturdays whereas the largest scatter and most of the data with high toluene to benzene ratios were observed on weekdays. Until now, the weekend effect for ozone (partly in combination with other air pollutants like CO and total VOCs) is well documented (BRÖNNIMANN & NEU, 1997; DIEM, 2000; JENKIN ET AL., 2002; MARR & HARLEY, 2002; HEUSS ET AL., 2003). However, there are only a few studies on the weekend effect on certain VOC species. BLANCHARD &
Table 4.1: Mean afternoon (10 AM to 6 PM) toluene and benzene mixing ratios (in ppb), and toluene to benzene ratios for July and August. %: obtained from the Direzione Generale Qualità dell'Ambiente, Lombardia, *: 22 July to 04 August 2002, †: 05 August to 25 August 2002. Como, Monza, and Milano data were available from 1996 - 2003, 2000 - 2003, and 2001 - 2002, respectively.

<table>
<thead>
<tr>
<th>Station</th>
<th>July tol</th>
<th>July benz</th>
<th>July tol/benz</th>
<th>August tol</th>
<th>August benz</th>
<th>August tol/benz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Como%</td>
<td>8.5</td>
<td>1.9</td>
<td>4.8</td>
<td>6.6</td>
<td>1.5</td>
<td>4.4</td>
</tr>
<tr>
<td>Monza%</td>
<td>7.5</td>
<td>1.5</td>
<td>7.1</td>
<td>4.7</td>
<td>1.1</td>
<td>5.3</td>
</tr>
<tr>
<td>Milano%</td>
<td>3.9</td>
<td>1.1</td>
<td>3.5</td>
<td>2.4</td>
<td>0.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Verzago</td>
<td>0.8*</td>
<td>0.3*</td>
<td>3.9*</td>
<td>0.6†</td>
<td>0.3†</td>
<td>2.3†</td>
</tr>
</tbody>
</table>

TANENBAUM (2003) showed for 10 sites in California that the benzene and toluene levels are considerably reduced on weekends, especially on Sundays. Figure 4.4b nicely reveals that a 'weekend effect' in the toluene to benzene ratios can be detected despite the limited number of data during a 70-day field campaign.

Figure 4.5a shows a corresponding plot to Figure 4.1 for mid-August 2002. In contrast to 1998, the VOCs were measured by PTR-MS. The black horizontal bars stress the periods with the conditions that prevailed in 1998 when toluene peaks around noontime occurred. It is obvious that on average no similar behavior could be detected within the presented period except at the end of the 2002 campaign, when such peaks were observed again as it is seen in Figure 4.5b. That seems to be a result of the 'ferragosto', the Italian vacation time effect in mid-August, when industrial activities and traffic are considerably reduced because by the end of August the vacation time is terminated in this area. This effect is also corroborated by different slopes of the toluene versus benzene plot that reveals the different conditions during the 3 weeks in mid-August (see Figure 4.6). The slopes at the beginning and at the end of August are nearly identical whereas the slope in between is considerably lower. The meteorological conditions were at least similar during the first and the second period and no considerably different ozone levels were found. Therefore a strong bias due to different photochemical oxidation capacities of the atmosphere is not expected. Consequently, a different emission pattern (due to different industrial activities) is likely to be responsible for the different toluene to benzene ratios. The mean toluene/benzene ratios are 3.9, 2.7, and 3.2 for the first, the second, and the third period, respectively. Perennial benzene and toluene data from the Direzione Generale Qualità dell’Ambiente, Regione Lombardia for measurement sites close to traffic emissions in the Po Basin show considerably reduced benzene and toluene mixing ratios in August, too, as well as significant changes (> 99.9%; two-population (independent) t-test) in the toluene to benzene ratio.
Figure 4.6: Toluene to benzene scatterplot for the 2002 campaign. Different periods are characterized by different symbols. The slopes of the orthogonal regression line are 5.3 for the first ($R^2 = 0.36$; solid black line) and the third period ($R^2 = 0.40$; dashed black line) and 2.5 for the second period ($R^2 = 0.43$; grey line).

Similar to the ones observed at Verzago. The mean afternoon (10 AM to 6 PM) benzene and toluene mixing ratios dropped in Como (Viale Cattaneo), Monza (Via Elvezia), and Milano (Via de Vincenti) from July to August as listed in Table 4.1. At Verzago, the mean benzene ratios were already low in July and no reduction in the mean benzene was observed. The slightly smaller decrease of the ratio at the three traffic dominated sampling sites compared to our semi-rural site could be explained by a more dominating industrial impact (including a reduced industrial impact in mid-August) at Verzago.

Table 4.2 summarizes a compilation of toluene to benzene ratios at Verzago for the three campaigns and the two different effects discussed above. On the one hand, the lowest toluene to benzene ratios were always measured on Sundays, and the highest on weekdays. On the other hand, the toluene to benzene ratios in mid-August 2002 were similar on weekdays and on weekends, confirming the reduced industrial emissions during that month.

4.3.2 Cyclohexane

Another compound of industrial origin was detected in 2003 (Figure 4.7). During most of the nights, distinct cyclohexane peaks up to 9 ppb appeared between 9 and 10 PM whereas levels usually below 500 ppt were observed during the rest of the day.
Table 4.2: Mean (± standard error of the mean) toluene to benzene ratios at Verzago on weekdays, Saturdays, and Sundays for the three different campaigns. The campaign in 2002 is additionally split into two periods to emphasize the 'ferragosto effect'.

<table>
<thead>
<tr>
<th>campaign</th>
<th>weekday</th>
<th>Saturday</th>
<th>Sunday</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIPAPO 1998</td>
<td>3.77 ± 0.04</td>
<td>2.84 ± 0.07</td>
<td>2.30 ± 0.03</td>
</tr>
<tr>
<td>FORMAT 2002, all</td>
<td>3.23 ± 0.06</td>
<td>2.89 ± 0.08</td>
<td>2.57 ± 0.07</td>
</tr>
<tr>
<td>FORMAT 2002, 05.08. to 25.08.</td>
<td>2.73 ± 0.06</td>
<td>2.87 ± 0.10</td>
<td>2.50 ± 0.08</td>
</tr>
<tr>
<td>FORMAT 2002, rest</td>
<td>3.93 ± 0.09</td>
<td>2.92 ± 0.12</td>
<td>2.66 ± 0.10</td>
</tr>
<tr>
<td>FORMAT 2003</td>
<td>3.35 ± 0.11</td>
<td>3.21 ± 0.11</td>
<td>2.13 ± 0.08</td>
</tr>
</tbody>
</table>

No peaks were measured at weekends, which points again to an industrial release. Cyclohexane is used for the production of synthetic fibers and as a solvent in varnishes, resins, and stain removers. Figure 4.8 shows the correlation between the wind conditions and the cyclohexane mixing ratios. It reveals that the point source is located in the north and the mixing ratios are advected most efficiently with wind speeds between 2 and 3 m/s. In contrast to peaks of ethene and propene coincident with the turn of the wind direction from west to north (see the companion paper (Steinbacher et al., 2004)), the cyclohexane peaks appeared around 1 to 2 hours after the change of the wind direction showing that sources for cyclohexane and the alkenes were different. Like the source of the alkenes, the emission source of cyclohexane is also located in the north. The short and narrow peaks of cyclohexane suggest a point source within a couple of kilometers, most probably between the sampling site and the Alpine foothills in the north. Assuming a wind speed of 1.5 m/s and considering the time of 1 to 2 hours after the wind turn, the maximum distance is 10 km. It points to a periodical short-term release of cyclohexane possibly at the end of a production process.

4.3.3 Receptor modeling using positive matrix factorization analysis

A multivariate receptor model was employed for air pollution concentration apportionment. Such statistical analysis allows to attribute the variabilities of trace gas measurements to different concentration profiles. The commonly used method of Chemical Mass Balance models needs a priori knowledge of the individual source profiles, which is often not available (Watson et al., 2001). Here we use so called ‘Positive Matrix Factorization’ (PMF), a variant of factor analysis with non-negative factor elements (Paatero & Tapper, 1994; Paatero, 1997) in order to analyze the measurements of 2003. The results indicate that five different pro-
Figure 4.7: Time series of cyclohexane at Verzago measured with GC-FID in 2003. Weekends are marked with ellipses.

Figure 4.8: Scatterplot of cyclohexane versus wind direction (big panel) and wind speed (small panel) for the 2003 field campaign.
4.3. Results and Discussion

Figure 4.9: Concentrations profiles of the Positive Matrix Factorization analysis applied to the VOC dataset measured in 2003. Methylpentane represents the sum of 2-methylpentane and 3-methylpentane.

Figure 4.10: Mean diurnal cycle of the profile contributions for the period from September 17 to 23, 2003.
files were required to fit the field measurements to identify and distinguish various striking concentration profiles (see Figure 4.9). Concentration profile #5 is obviously determined by the cyclohexane concentration. This profile does not contain any substantial contribution of another species, revealing that only cyclohexane is emitted by this certain industrial process. The diurnal pattern of the contribution to profile #5 (see Figure 4.10) nicely represents the diurnal cyclohexane pattern. Concentration profile #2 is the only profile with a substantial isoprene concentration. As the diurnal cycle of the contribution to profile #2 (see Figure 4.10) looks quite similar to the real isoprene cycle (see the companion paper (STEINBACHER ET AL., 2004)), this profile can be attributed to a biogenic impact. Profile #3 is identified as the vehicle exhaust (tailpipe) concentration profile. It shows a toluene to benzene ratio of 2.5 (in good agreement with the Sunday toluene/benzene traffic ratio, see Table 4.2), and a high ethane, ethyne, and propene concentration that is characteristic for vehicle exhaust emissions (BORBON ET AL., 2003). The lower toluene to benzene ratios compared to the data observed at Bresso reveal that photochemically aged air masses are predominantly analyzed at Verzago. Furthermore, the profile contribution is significantly correlated with carbon monoxide (CO) ($R = 0.73, n = 315$), a good marker for traffic emissions that was not included in the PMF analysis. The profiles #1 and #4 only differ by the high toluene contribution in #4 and the different diurnal pattern. Profile #1 decreases in the afternoon while profile #4 increases. Therefore we attribute profile #1 to a constant emission source whereby the diurnal variation reflects the inverse daily cycle of the mixing height. The composition of profile #1 is indicative of natural gas leakages as it was also shown by studies in the United Kingdom and the United States (DERWENT ET AL., 1995, 2000; CHOI & EHRRMAANN, 2004). The high toluene concentration in profile #4 and the apparently enhanced emissions in the afternoon point to industrial activities. Since also evaporative losses from gasoline might be higher in the afternoon due to higher temperatures, we interpret this profile as a mixture of industrial activities (solvent use, combustion) and partly non-tailpipe emissions (evaporation) of gasoline. In summary, the 5 different profiles could be reasonably related to different processes: profile #1 (natural gas), profile #2 (biogenic impact), profile #3 (vehicle exhaust), profile #4 (industry; solvent use and combustion, non-tailpipe evaporation), profile #5 (cyclohexane).

Figure 4.11 shows the diurnal cycles of the profile contributions and $NO_x$, separated into weekday and Sunday data. For the weekday data, average diurnal cycles were calculated for the period from September 17 to 23 as the meteorological conditions for this period were similar to the meteorological conditions on the two Sundays. Substantial differences occurred for profile #5 as the cyclohexane peaks were only detected on weekdays and less significantly for profile #4 during the daytime hours as the industrial influence ceased on Sundays. For profile #3 and $NO_x$ (a marker for combustion processes, especially diesel vehicles) a considerable difference was found in the morning hours whereas no clear difference appeared in
4.3. Results and Discussion

Figure 4.11: Diurnal cycles of the profile contributions #1 to #5 and NO\textsubscript{x} during September 2003 at Verzago. 'Weekday 17 to 23 September' reflects the data from Wednesday 17 to Friday 19 and Monday 22 to Tuesday 23. 'Sunday' represents the data on 21 and 28 September. Vertical bars represent the standard deviations of the mean. Due to the small number of data, no variability is shown for Sunday data.
the evening hours for the two selected periods. This agrees with the analyses of Blanchard & Tanenbaum (2003) for NO\textsubscript{x}, benzene, and toluene mixing ratios on Sundays and weekdays. Our findings are also in line with traffic statistics in Milan for summer months (Agenzia Regionale per la Protezione dell’Ambiente della Lombardia Dipartimento, Milan), which show that for four counting locations there are on average 3.3 times more cars (< 7 m length) on weekdays than on Sundays in the morning, but only 1.4 times more in the evening. The number of trucks and busses (> 14 m) is even reduced a factor of 5.5 in the morning and 2.4 in the evening. This implies that the various weekday to Sunday differences in both the profile contribution #3 and the NO\textsubscript{x} mixing ratios are driven by different traffic densities.

### 4.4 Conclusions

Three measurement campaigns within a period of 5 years were performed in the Po Basin in early summer 1998, summer 2002, and autumn 2003. Measurements of aromatic compounds at Verzago showed a recurrent feature with enhanced toluene peaks without enhanced concentrations of benzene at around noontime. Closely correlated benzene to toluene ratios in car exhausts and the absence of toluene peaks during weekends and the holiday period in summer pointed to an advection of industrially released toluene. Different toluene to benzene ratios on weekends compared to weekdays as well as in August compared to July and September enabled us to identify a 'weekend effect' and a 'vacation (ferragosto) effect', respectively. Cyclohexane measurements revealed another anthropogenic impact at the semi-rural sampling site. Distinct peaks appeared between 9 and 10 PM under northerly winds and wind speeds between 2 and 3 m/s. No peaks were observed on Saturdays and Sundays. A multivariate receptor model analysis for the semi-rural site in 2003 distinguished five different concentration profiles that could be reasonably attributed to natural gas, biogenic impact, vehicle exhaust, industrial activities, and a single cyclohexane source. Diurnal cycles of the profile contribution showed characteristic differences on weekdays and Sundays. The vehicle exhaust profile contribution was in line with traffic statistics and could be reasonably explained by traffic densities.

The selected VOCs presented here and in a companion paper (Steinbacher et al., 2004) illustrated the anthropogenic and biogenic impact on the ambient trace gas levels in the Po Basin. These detailed analyses will provide a good basis within the FORMAT project to investigate the production of formaldehyde from different VOCs and the role of formaldehyde as an intermediate of the VOC oxidation in the boundary layer.
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References


References


References 93


Chapter 5

Volatile organic compounds in the Po Basin. Part B: biogenic VOCs

submitted for publication in the Journal of Atmospheric Chemistry

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Abstract Measurements of volatile organic compounds (VOCs) were performed in the Po Basin, northern Italy in early summer 1998, summer 2002, and autumn 2003. During the three campaigns, trace gases and meteorological parameters were measured at a semi-rural station, around 35 km north of the city center of Milan. Bimodal diurnal cycles of isoprene with highest concentrations in the morning and evening were found and could be explained by the interaction of emissions, chemical reactions, and vertical mixing. The diurnal cycle could be qualitatively reproduced by a three-dimensional Eulerian model. The nighttime decay of isoprene could be attributed mostly to reactions with NO\textsubscript{3}, while the decay of the isoprene oxidation products could not be explained with the considered chemical reactions. Methanol reached very high mixing ratios, up to 150 ppb. High concentrations with considerable variability occurred during nights with high relative humidities and low wind speeds. The origin of these nighttime methanol concentrations is most likely local and biogenic but the specific source could not be identified.

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95
5.1 Introduction

Volatile organic compounds (VOCs) play a central role in the photochemistry of the atmospheric boundary layer. VOCs, carbon monoxide (CO), and nitrogen oxides (NO$_x$) are the precursors of the tropospheric ozone (O$_3$) production. In the urban and semi-urban planetary boundary layer, O$_3$ production is usually limited by the availability of VOCs. Biogenic VOCs can play an important role in regional photochemistry and O$_3$ formation by reducing the OH concentration in clean air masses and increasing the peroxy radical concentration that results in an imbalance in the photostationary steady state (FEHSENFELD ET AL., 1992; TRAINER ET AL., 1987). Even in some urban atmospheres in the United States, the biogenic emissions cannot be neglected in respect of photochemical smog formation (CHAMEIDES ET AL., 1988). However, biogenic VOC species cannot be reduced through emission controls as other anthropogenic compounds. Therefore, rising attention was given to emissions of biogenic VOCs and their oxidation processes in the last years. Due to its high reactivity, especially isoprene (CH$_2$=C(CH$_3$)CH=CH$_2$; 2-methyl-1,3-butadiene) and its oxidation products (methyl vinyl ketone and methacrolein) were in the focus of interest (BIESENTHAL ET AL., 1997, 1998; STARN ET AL., 1998; CURREN ET AL., 1998; STROUD ET AL., 2001; HURST ET AL., 2001). Isoprene plays an important role in the production of O$_3$ not only in rural environments but also in anthropogenically influenced atmospheres (BIESENTHAL ET AL., 1997). Measurements in Northern Italy over the whole year 2000 showed that the isoprene photooxidation contributed in summer 30 to 60% to the ambient formaldehyde concentrations and 50 to 75% to the local O$_3$ formation (DUANE ET AL., 2002). The general effect of biogenic VOCs on the tropospheric chemistry in Spain and for the Greater Paris Area was investigated by THUNIS & CUVELIER (2000) and DEROGNAT ET AL. (2003), respectively. While the biogenic emissions contributed 10 ppb O$_3$ for the case study in Spain, the analysis in France showed up to 40 ppb O$_3$ produced due to biogenic VOC emissions for an extreme day. Airborne VOC measurements in the metropolitan area of Milan showed that isoprene contributes only less than 10% to the total VOC reactivity (DOMMEN ET AL., 2002).

Apart from isoprene and methane, methanol (CH$_3$OH) is one of the species with the highest carbon turnovers in the atmosphere. Due to its high atmospheric concentrations, methanol can act at least locally as a substantial sink for hydroxyl radicals despite the slow reaction rate constant with OH. Via H-atom abstraction and subsequent reaction with O$_2$, methanol is moreover a direct precursor of formaldehyde (SEINFELD & PANDIS, 1998). The lifetime of methanol due to reaction with OH is 12 days (ATKINSON, 2000). Because of the slow reactions of methanol in the gas phase, dry and wet deposition also become important sinks of this species.

The measurements discussed here were performed within the scope of the field experiment Pianura Padana Produzione di Ozono (PIPAPO; ozone production in
5.2. Sampling site and instruments

Biogenic VOC measurements were conducted during all three campaigns at Verzago-Alzate, around 35 km north of the city center of Milan. The measurement containers were placed at the border of a corn field. Corn is known to be a non-isoprene emitter (LAMB ET AL., 1993) or at most a very weak isoprene source (PLASS-DÜLMER ET AL., 1998). A recent publication dealing with air-surface exchanges over corn showed that the majority (around 75%) of the VOC emissions can be related to methanol (DAS ET AL., 2003). No significant isoprene emission was detected in their study. The closest forest considering as an isoprene source was located approximately 200 to 300 m in southerly and westerly direction. A high-resolution emission inventory for a weekday in May 1998 for the Po Basin revealed that biogenic emissions are only significant during the sunlight hours and stationary anthropogenic sources dominate the VOC emissions whereas the traffic emissions contribute half as much (DOMMEN ET AL., 2003).

An Airmotec HC1010 gas chromatograph (KONRAD & VOLZ-THOMAS, 2000) with flame ionization detector (GC-FID) (ChromatoSud, Saint Antoine, France) was used in 1998 and 2002 to measure hydrocarbons between C4 and C10. Laboratory test with added ozone indicated that ozone up to mixing ratios of 180 ppb do not cause sampling artifacts in the used analytical system (GRÜEBLER, 1999). A proton transfer reaction mass spectrometer (PTR-MS) was used at Verzago in 2002 for measuring the most common atmospheric VOCs excluding the alkanes and small alkenes/alkynes (LINDINGER ET AL., 1998; STEINBACHER ET AL., 2003). With this measurement technique, VOCs are measured at their parent mass + 1, resulting in an isoprene signal at m/z 69, a signal of methyl vinyl ketone + methacrolein (both with a parent mass of 70 amu) at m/z 71, and methanol at m/z 33. Another GC-FID system (Varian 3400) was operated in 2003 to measure hydrocarbons from C2 to C7. Meteorological parameters like temperature, wind speed and direction, humidity, and radiation as well as inorganic species like ozone, carbon monoxide, and nitrogen oxides were also measured during the three campaigns. A more detailed description of the aims of the projects, the measurement sites, the instrumental equipment, meteorological conditions, and ozone concentrations is given in the companion paper (STEINBACHER ET AL., 2004).
5.3 Results and discussion

5.3.1 Isoprene, methyl vinyl ketone, and methacrolein

Interpretation of diurnal cycles

Figure 5.1 shows a typical time series of isoprene (measured with PTR-MS as protonated mass 69), the estimated isoprene emissions according to the Guenther algorithm (GUENTHER ET AL., 1993), and the sum of the main isoprene oxidation products methyl vinyl ketone and methacrolein (both measured at protonated mass 71) for a period in 2002. Similar diurnal variations of isoprene were found in the measurements during summer 1998 (GRÜEBLER, 1999). The Guenther algorithm considers the isoprene emissions only as a function of light and temperature due to the light- and temperature-dependent activity of the isoprene producing enzyme. SIMPSON ET AL. (1995) stated that the applicability of the algorithm to European conditions needs to be checked due to the different climatic conditions in the U.S. and in Europe. STEINBRECHER ET AL. (1997) compared measured isoprene emissions with the simulated ones and concluded that the algorithm is able to predict the isoprene emissions for the Mediterranean area within an uncertainty of 50%.

Isoprene reacts rapidly with OH, O₃, and NO₃. The first generation products are methyl vinyl ketone (CH₂=CHCOCH₃; MVK) and methacrolein (CH₂=C(CH₃)CHO; MACR) in addition to formaldehyde. MVK is favored by

![Figure 5.1: Isoprene mixing ratios (m/z 69), estimated isoprene emissions according to the Guenther algorithm (GUENTHER ET AL., 1993), and methyl vinyl ketone + methacrolein mixing ratios (m/z 71) for a 7-day period in 2002.](image-url)
5.3. Results and discussion

Table 5.1: Yields of MVK and MACR and the ratio of the yields from isoprene oxidation due to reactions with OH radicals, O₃, and NO₃ radicals (Kwok et al., 1996, and references therein) and the rate constants k (in cm³ molecule⁻¹ s⁻¹) for isoprene with the reactants at 25 °C (Atkinson & Arey, 2003).

<table>
<thead>
<tr>
<th>reactant</th>
<th>MVK</th>
<th>MACR</th>
<th>ratio</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>0.32</td>
<td>0.23</td>
<td>1.4</td>
<td>1.0·10⁻¹⁰</td>
</tr>
<tr>
<td>O₃</td>
<td>0.16</td>
<td>0.39</td>
<td>0.4</td>
<td>1.3·10⁻¹⁷</td>
</tr>
<tr>
<td>NO₃</td>
<td>0.035</td>
<td>0.035</td>
<td>1.0</td>
<td>6.8·10⁻¹⁵</td>
</tr>
</tbody>
</table>

oxidation with OH radicals whereas more MACR is produced when isoprene reacts with O₃. The reported yields are summarized in Table 5.1. Chemical lifetimes of isoprene, MVK, and MACR due to the reaction with OH radicals are 1.4 h, 6.8 h, and 4.1 h, respectively, assuming a OH radical concentration of 2.0·10⁶ molecule cm⁻³ (Atkinson, 2000).

Recent studies have reported an anthropogenic fraction of isoprene attributed to traffic (Reimann et al., 2000; Borbon et al., 2001). From correlation analysis of field measurements at Bresso, a sub-urban site close the city center of Milan, Gru¨ebler (1999) concluded that in summer approximately 50% of isoprene originated from road traffic. The anthropogenic fraction of isoprene can be estimated out of a usually good correlation with 1,3-butadiene. 1,3-butadiene measured with the GC-FID system in 2003 was on average below 100 ppt. Reimann et al. (2000) reported for measurements on the Swiss Plateau in winter an (anthropogenic) isoprene to 1,3-butadiene ratio of 0.4. A similar analysis in France resulted in an (anthropogenic) isoprene to 1,3-butadiene ratio of 0.3 (Borbon et al., 2001). Therefore, the evening isoprene mixing ratios at Verzago with peaks of up to 3 ppb in 2003 (see Figure 5.3) are not of anthropogenic origin.

Figure 5.1 reveals that the measured isoprene mixing ratios cannot be explained when only considering the expected isoprene emissions. In the morning, the isoprene levels are rising with the start of the emissions but drop after 2 to 3 hours and rise again in the late afternoon for a period of around 2 hours. Thereafter, the isoprene concentrations suddenly decrease. Several other publications reported a similar bimodal diurnal cycle of isoprene with peaks in the morning and in the evening (Curren et al., 1998; Starn et al., 1998; Reimann et al., 2000).

This characteristic pattern suggests an interplay between photochemical and dynamical processes. In the morning, the OH concentrations, the mixing height and the vertical mixing are low, and the isoprene mixing ratio first increases with increasing isoprene emissions. Later, OH production from ozone photolysis is enhanced, and the mixing height increases, incorporating residual layer air with lower isoprene concentrations into the boundary layer. Both effects lead to an isoprene decrease at around 11 AM. In the evening, isoprene is still emitted, and the lower
OH radicals and the lower vertical mixing result in an increase in isoprene concentrations. As soon as the ground becomes colder than the air above, the stable nocturnal boundary layer arises and a distinct accumulation of isoprene occurs. The evening isoprene maxima at Verzago emerge when the estimated isoprene emissions nearly cease. This can only partially be explained by the distance of 200 to 300 m between the sampling site and isoprene emitters and the time needed to advect the air masses from the forest to our instrument inlet. The mixing height in these evening hours must indeed be very low. After sunset, isoprene emissions vanish and isoprene mixing ratios decline due to chemical reactions with NO₃, O₃, and OH (OH could originate from alkene ozonolysis in the dark), and due to an increase of the wind speed (see Figure 5.2) resulting in a more efficient vertical and horizontal mixing. Typical OH concentrations during the night are up to 2 orders of magnitude smaller in the night than during the day (e.g. PLASS-DÜLMER ET AL., 1998). The oxidation products (MVK and MACR) are increasing shortly after the morning isoprene peak (Figure 5.1). This suggests that isoprene photooxidation is, together with the enhanced vertical mixing and dilution, responsible for the drop in the isoprene signal in the late morning. The concentration of the primary oxidation products also decreases around noon that again can be explained by further photooxidation and stronger vertical mixing. In contrast to the morning, the evening peak of isoprene is not followed by a peak of MVK + MACR indicating an isoprene decay due to the reaction with NO₃ or due to dynamic processes. The relevant nighttime processes will be discussed in more detail later in this section.

MVK + MACR to isoprene ratio

Figure 5.2 illustrates the diurnal cycles of the ratio of the oxidation products MVK + MACR to isoprene, nitrogen oxides, wind speed, and temperature at Verzago for the fair weather period from August 12 to 22, 2002. We detected low ratios around 8.30 AM and 7.30 PM, and higher values during the day and during nighttime. The MVK + MACR to isoprene ratio is partly driven by the OH chemistry that decomposes isoprene, and generates and destroys MVK and MACR at the same time. Photolysis of MVK and MACR is 6 to 7 times slower than the oxidation due to the reaction with OH. Besides the oxidant chemistry, the ratio depends also on the isoprene emission strengths (and therefore on temperature and radiation), dynamic processes and the proximity of the sampling inlet to the isoprene source (BIESENTHAL ET AL., 1998; MONTZKA ET AL., 1995). Most of the diurnal cycles of this ratio published showed a different pattern with low ratios during the day and increased ratios in the night reflecting the diurnal isoprene emission profiles (BIESENTHAL ET AL., 1997, 1998; APEL ET AL., 2002). In contrast to that and in agreement with our data, MONTZKA ET AL. (1993, 1995) reported the highest isoprene concentrations in the early evening and the lowest (MVK+MACR)/isoprene ratios in the early morning and the evening.
5.3. Results and discussion

Yokouchi (1994) and Biesenthal et al. (1998) suggested a relationship between the (MVK+MACR)/isoprene ratio and the NO$_x$ concentration in the atmosphere. Since MVK and MACR are produced by the reaction of isoprene peroxy radicals with NO whereas the competing reaction of isoprene peroxy radicals with another (hydro or organic) peroxy radicals produces organic hydroperoxides, enhanced NO$_x$ levels up to 2 - 3 ppb could result in higher MVK and MACR yields. At higher NO$_x$ mixing ratios, the (MVK+MACR)/isoprene ratio decreases again with increasing NO$_x$ due to a limitation of OH by the reaction of OH with NO$_2$ forming (stable) HNO$_3$ molecules. The NO$_x$ mixing ratios at our sampling site were between 2 and 6 ppb, slightly above the suggested NO$_x$ optimum for the highest (MVK+MACR)/isoprene ratios. In agreement with Biesenthal et al. (1998), elevated NO$_x$ concentrations coincide with low (MVK+MACR)/isoprene ratios. This relation should be only important during the photoactive periods, i.e. during daytime. However, the most distinct anti-correlation was found in the morning and the evening hours when photochemistry is less important. During these hours, the isoprene and NO$_x$ mixing ratios show similar profiles with elevated values due to the accumulation of the emissions in a shallow boundary layer. Most of all emissions and reduced vertical mixing determine the concentrations during this time. An analysis restricted to afternoon periods showed no relation between the (MVK+MACR)/isoprene ratio and the NO$_x$ concentrations possibly due to the small variability range of the NO$_x$ mixing ratios. It is therefore difficult

![Figure 5.2](image_url)

Figure 5.2: Mean daily cycles of the (MVK+MACR) to isoprene ratio, the NO$_x$ mixing ratios, the wind speed, and temperature at Verzago for August 12 to August 22, 2002. The bars denote the standard deviations of the mean.
to evaluate the validity of the suggestion of Yokouchi (1994) and Biesenthal et al. (1998).

The wind speed is low in the early morning and late evening hours suggesting a reduced mixing when the mixing layer and the stable nocturnal boundary layer, respectively, start to develop. Low wind speeds cause less efficient horizontal mixing and also less turbulent conditions with reduced vertical mixing. But most of all, the vertical mixing is driven by convection. As the convection is strongest when the temperature at the ground is high, the temperature can be used as a rough measure for thermal convection. Lowest (MVK+MACR)/isoprene ratios, and highest NO\textsubscript{x} mixing ratios were measured when the lowest temperatures at the ground were observed.

At our sampling site the next major isoprene sources are approximately 200 - 300 m away, and therefore the (MVK+MACR)/isoprene ratio is driven by photochemistry (as seen in Figure 5.1 with the highest MVK+MACR ratios slightly after the morning isoprene peak) as well as by dynamic processes (as seen in Figure 5.2 with the lowest (MVK+MACR)/isoprene ratios in the morning and evening hours with low wind speed and temperature).

**Isoprene nighttime chemistry and dynamics**

Figure 5.3 shows an 8-day time series of isoprene, wind speed and direction, and two alkenes at Verzago in September 2003. The morning peaks were less pronounced and the evening peaks were shorter compared to 2002, but the diurnal bimodal isoprene cycle was similar to 2002 and 1998 (not shown) despite reduced isoprene emissions in fall compared to summer. Stable meteorological conditions led to a recurrent daily pattern of isoprene, wind, and other VOCs between September 17 and 21. Usually, the wind speed was reduced in the afternoon simultaneously with a stable wind direction from SSW and in coincidence with elevated isoprene levels. Between 6 and 7 PM, the wind direction switched abruptly from SSW to N followed by a sudden decrease of the isoprene signal and an increase of ethene and propene. Isoprene-depleted and more polluted air from the vicinity north of the sampling site suggested a change of the air mass. During the night, the wind direction remained north and the alkene mixing ratios decreased again due to cleaner air advection from the Alpine foothills located around 5 km north of Verzago. Based on this case study, a dominant dynamic influence on isoprene seems to be likely.

Figure 5.4 demonstrates typical decays of isoprene mixing ratios for the 2002 campaign at Verzago. In the majority of cases, an exponential decay (illustrated by a linear decay using a logarithmic scale) points to a (pseudo-)first order decay mechanism. The isoprene lifetime can be calculated from the negative slope on a logarithmic scale. For the presented days, lifetimes vary between 1.7 and 2.9 hours. A summary of all isoprene lifetimes calculated from the exponential decay is given in Table 5.2. The number of representative decays is smaller in 2003, due to both
5.3. Results and discussion

Table 5.2: Mean isoprene lifetimes (in hours), standard deviations, and minimum and maximum lifetimes for selected days with a representative isoprene decay (# of data points ≥ 5, R² ≥ 0.85).

<table>
<thead>
<tr>
<th>year</th>
<th># of days</th>
<th>average</th>
<th>stdev</th>
<th>min</th>
<th>max</th>
</tr>
</thead>
<tbody>
<tr>
<td>1998</td>
<td>17</td>
<td>1.7</td>
<td>0.44</td>
<td>0.9</td>
<td>2.5</td>
</tr>
<tr>
<td>2002</td>
<td>12</td>
<td>2.04</td>
<td>0.64</td>
<td>0.8</td>
<td>3</td>
</tr>
<tr>
<td>2003</td>
<td>7</td>
<td>1.92</td>
<td>0.83</td>
<td>1</td>
<td>3.3</td>
</tr>
</tbody>
</table>

the lower time resolution of the VOC measurements and the selection criteria of more than 4 data points and R² higher than 0.85 for the considered nights. In total, lifetimes are between 0.8 and 3.3 hours, in a good agreement with published data of BIESENTHAL ET AL. (1998) (1 - 3 hours), HURST ET AL. (2001) (2 - 5 hours), and APEL ET AL. (2002) who distinguished between the nighttime data (lifetime of ca. 0.75 hours) and after 9.30 PM (lifetime around 3.6 hours).

In the next step of our analysis, we assumed that the decrease in isoprene concentration is entirely caused by the reaction with NO₃. We considered a reaction rate constant of 6.54·10⁻¹³ cm³ molecule⁻¹ s⁻¹ at 18 °C, and calculated the hypothetical constant NO₃ mixing ratio needed to fit the measurements. For the mean lifetimes in 1998, 2002, and 2003, we received mean NO₃ mixing ratios of 10.9 ppt, 9.6 ppt, and 10.5 ppt, respectively. In total, the mixing ratios ranged from 23.0 ppt.

Figure 5.3: Time series of isoprene, wind speed, wind direction, ethene, and propene during the 2003 campaign. The dashed lines denote the isoprene maxima to aid visual inspection of the data.
Chapter 5. Biogenic VOCs in the Po Basin

Figure 5.4: Typical nighttime isoprene decays at Verzago in summer 2002.

(lifetime of 0.8 hrs) to 5.2 ppt (3.3 hrs). These values seem reasonable.

No NO3 measurements were performed during the three campaigns. As the sink mechanisms of NO3 could not be properly estimated due to the unknown loss terms like hydrolysis and deposition of N2O5 as well as gas phase reactions of NO3 with not measured VOC species (e.g. monoterpenes) (GEYER ET AL., 2001), an estimation of NO3 assuming equilibrium conditions is highly uncertain. However, we analyzed the variability of NO3 in view of the NO3 production rate due to the reaction of NO2 with O3. Figure 5.5 shows a scatterplot of the NO3 mixing ratios derived from the nighttime isoprene slopes versus the mean NO3 production rates during the same periods. A correlation between the NO3 production rate and the NO3 mixing ratios, indirectly derived by fitting the isoprene measurements, is present. Enhanced production rates in common with higher NO3 mixing ratios and subsequently shorter isoprene lifetimes are visible despite uncertainties and variabilities of the measured isoprene decay and the variability of the production rates. The scatter might be related to other influencing processes such as horizontal advection of air masses with other isoprene contents or vertical dispersion of the measured air masses with isoprene depleted air. Lowest NO3 values were derived for the 2002 campaign due to less polluted boundary layer conditions and thus lower NO2 and O3 concentrations as a consequence of reduced anthropogenic activities during August as described in the companion paper (STEINBACHER ET AL., 2004).
5.3. Results and discussion

Figure 5.5: NO₃ mixing ratio derived from the isoprene slopes vs. the estimated NO₃ production rates for 1998, 2002, and 2003. Open symbols represent data that are based on slopes with less than 5 data points or $R^2$ of < 0.85. Vertical and horizontal bars represent the errors of the slope and the standard errors of the average NO₃ production rate, respectively. Labeled data are also illustrated in Figure 5.7.

The isoprene decay that led to the data point with nearly 40 ppt of NO₃ was at least partly influenced by a change of the air mass. This was corroborated by an ozone mixing ratio increase from 40 to 60 ppb between 8 and 9 PM. Excluding this data point, the correlation coefficient R is 0.69, suggesting an important influence of NO₃ chemistry on the isoprene decay at this semi-rural site.

Figure 5.6 presents the corresponding plots to Figure 5.4 for the sum of the two oxidation products. An exponential decay could not be detected every night, but was still frequently observed. Assuming chemical reactions as the dominant pathway of the observed decrease in MVK + MACR (in a similar way as described above), the calculated concentrations of OH and NO₃ would be unrealistically high, much higher than required to explain the isoprene decrease. Apart from that, such high OH concentrations would result in a considerable isoprene degradation leading again to a formation of these oxidation products. Therefore, a chemical explanation for the nighttime decay of MVK + MACR could not be found.

Additionally, we performed a sensitivity analysis with a box model to gain further insight into the nocturnal behavior of isoprene and the oxidation products. For this purpose, the Master Chemical Mechanism (MCM), version 3, a freely downloadable model (http://chmlin9.leeds.ac.uk/) (JENKIN ET AL., 1997, 2003; SAUNDERS ET AL., 2003) was used. It is a nearly explicit mechanism with more than 12 600 reactions and more than 4 300 species. Here, only a reduced mechanism for the
isoprene degradation including the whole set of inorganic reactions was taken into account. Two reactions representing the homogeneous hydrolysis of N$_2$O$_5$ with one and two H$_2$O molecules were added to the mechanism (FINLAYSON-PITTS & PITTS Jr., 2000). Figure 5.7 shows the results of the box model simulations and the corresponding measurements of isoprene for four nights. MVK+MACR model results and measurements were included when available. The measured mixing ratios of isoprene, NO, NO$_2$, O$_3$ (and MVK+MACR when available) at the beginning of the isoprene drop were used as the starting conditions of the model. NO$_2$ and O$_3$ were constrained to the measurements during the whole simulation. Three different loss frequencies were used in the model to account for the uncertainty of the reaction of N$_2$O$_5$ on aerosol surfaces. GEYER ET AL. (2001) estimated from measurements near Berlin a variability of loss rates between 0.3-10$^{-4}$ and 22-10$^{-4}$ s$^{-1}$. Three different loss frequencies were used in our model simulations to account for the uncertainty of the reaction of N$_2$O$_5$ on aerosol surfaces. These were the default loss rate of the MCM (4-10$^{-4}$ s$^{-1}$), as well as a lower (1-10$^{-4}$; 'loss rate/4') and a higher (12-10$^{-4}$ s$^{-1}$; 'loss rate*3') rate. Figure 5.7a shows the night of June 4, 1998, a case with a high aerosol loading in the atmosphere. In agreement to that, the model fits best with the results when using the highest N$_2$O$_5$ loss rate, whereas on June 21, 1998 (panel b), the model can not reproduce the strong isoprene decay at all. This points to a significant dynamic influence (e.g. due to the advection
5.3. Results and discussion

Figure 5.7: Measured and modeled decay of isoprene on four nights. Measured and model decay of MVK + MACR are included for 2002. Modeled data are based on a box model with different N₂O₅ loss rates.

of less biogenically influenced air masses) that can not be considered by the box model. In contrast to other nights, wind speed higher than 3 m/s occurred during this period. For the case in 2002 (Figure 5.7c), the model run with the highest loss rate can again nicely reproduce the isoprene decay, whereas the decay of the oxidation products can not be reproduced in accordance with the analysis already undertaken when discussing the exponential MVK+MACR decays. In disagreement to the measurements, the MVK+MACR level even increased due to a slight generation of the oxidation products during the isoprene degradation. For the last case (Figure 5.7d), the model run with the default loss rate can explain the measured isoprene profile with concentrations close to the detection limit already 120 min after the start of the isoprene drop. It is possible to reproduce the decay chemically even if the low isoprene concentration after already 60 min might be due to a dynamic effect. These four cases reveal that the chemistry can often explain the isoprene decay when adapting the highly variable N₂O₅ loss rate. GEYER ET AL. (2001) attributed 42% of the NO₃ loss to the reaction of N₂O₅ with aerosols. These simulations support the simple approach presented in Figure 5.5. It seems that the main driving factor of the isoprene decay is chemistry. Only in selected cases, the dynamic processes might play a dominating role.
The contribution of vertical dispersion could only be estimated. During several nights in August 2002, the O₃ levels as well as temperatures stayed nearly constant beginning between 8.30 and 9.30 PM (indicated with arrows in Figure 5.8) and lasting several hours, whereas a substantial drop of both parameters could be observed before and after. It is known that O₃ concentrations considerably decrease during the night close to the ground due to dry deposition resulting in a vertical O₃ gradient. This 'step' in our temperature and ozone data could be explained by vertical mixing and downward transport of warmer and less O₃-depleted air. This mechanism could also explain the decay of both isoprene and MVK+MACR at night. Similar to the observations, one would expect a shorter lifetime of isoprene compared to MVK+MACR since the vertical gradient of isoprene, with its sources only at the ground, is usually more pronounced than that of the oxidation products, which can be produced in the whole boundary layer. But a weakness of this hypothesis concerns the good agreement of the measured and modeled isoprene series. The decay due to vertical dispersion has to be as strong as the expected chemical degradation so that the agreement of the model-measurement comparison would be fortuitous. Furthermore, assuming typical isoprene and O₃ gradients in the atmospheric boundary layer, it can be shown that the effect of the vertical mixing that is needed to maintain constant O₃ levels can only partly explain the observed isoprene decay.

The role that deposition plays at the sampling site is difficult to evaluate. O₃ is known for its potential to be substantially depleted due to dry deposition at night. As constant O₃ levels are often observed during the nighttime periods when

![Figure 5.8: 8-day time series of ozone and temperature in 2002. The arrows mark situations with stable temperature and ozone mixing ratios at night.](image-url)
the isoprene decays take place, the vertical mixing compensates the O\textsubscript{3} loss due to dry deposition. Deposition should be negligible for isoprene as it is a nonpolar compound. For the oxidation products MVK and MACR, deposition is a possible candidate for the decrease, because vertical mixing as well as chemistry failed. The MVK+MACR loss rate is in the same range as the estimated vertical mixing rate derived from the O\textsubscript{3} measurements and assumptions concerning mixing height (100 to 300 m) and O\textsubscript{3} deposition rate (0.5 cm/s). But consequently, negligible concentrations of MVK+MACR have to be assumed in the residual layer to attribute the whole decay to the vertical mixing.

The nighttime isoprene chemistry and dynamic was mostly studied in the United States (Biesenthal ET AL., 1998; Starn ET AL., 1998; Hurst ET AL., 2001; Falloona ET AL., 2001; Stroud ET AL., 2002; Sillman ET AL., 2002; Apel ET AL., 2002). As the sampling sites were in different environments, no consistent interpretation could be found within these publications. Measurements at remote-forested sampling sites led to the conclusions that OH was the most important oxidizing agent, whereas NO\textsubscript{3} played an unimportant role due to the low NO\textsubscript{x} levels (Biesenthal ET AL., 1998; Hurst ET AL., 2001; Falloona ET AL., 2001; Sillman ET AL., 2002). At sub-urban, semi-rural sites, or locations that are impacted by anthropogenic emissions, NO\textsubscript{3} dominates as the main chemical isoprene sink (Starn ET AL., 1998; Stroud ET AL., 2002, this study). Dynamics like horizontal advection and vertical dispersion have to be considered at every sampling site but can not be generalized as it was done for the chemical processes.

### 3-dimensional modeling of diurnal cycles of isoprene

A three-dimensional Eulerian model CAMx (Comprehensive Air Quality Model with Extensions) was used to simulate the diurnal cycle of isoprene. Figure 5.9 shows the results for May 13, 1998, an already well described case during the first intensive period of the PIPAPO campaign (Baertsch-Ritter ET AL., 2003, 2004; Andreani-Aksoyoglu ET AL., 2004). CAMX (Version 4), including the Carbon Bond Mechanism IV with an aerosol chemistry module, was used (Andreani-Aksoyoglu ET AL., 2004). The meteorology was preprocessed with the SAI Mesoscale Model (Baertsch-Ritter ET AL., 2004). The measured mixing ratios were lower in 1998 than in 2002 and 2003 due to still reduced emissions in May. However, the model slightly under-predicts the measurements. But the model nicely reproduced the measured bimodal diurnal isoprene cycle for 9 grid cells of 3 x 3 km size around Verzago. The highest isoprene levels shown here were simulated for the 3 grid cells north of Verzago, in agreement with the emission inventory that showed larger isoprene sources within the Alpine foothills region.
5.3.2 Methanol

We measured methanol mixing ratios with the PTR-MS during the 2002 campaign. The results for a 10-day period are presented in Figure 5.10 and show spike-like methanol plumes. Like isoprene, tropospheric methanol (CH$_3$OH) can be of anthropogenic and biogenic origin. The main global sources are biogenic emissions, chemical production in the atmosphere (GALBALLY & KRISTINE, 2002), biomass burning (HOLZINGER ET AL., 1999), emissions from dead plant material (WARNEKE ET AL., 1999), and primary anthropogenic sources (GOLDAN ET AL., 1995; HOLZINGER ET AL., 2001). Especially in summer, biogenic processes are by far the dominating sources (HOLZINGER ET AL., 2001). The emissions are affected by leaf temperature and stomatal conductance (MACDONALD & FALL, 1993) as well as by solar radiation (DAS ET AL., 2003). WARNEKE ET AL. (1999) reported enhanced methanol emissions of dead plant material after humidification in the laboratory. After getting wet, the VOCs attached to the cell structures dissolve in the water and are subsequently released to the atmosphere according to Henry’s law.

With a total average mixing ratio of 13.2 ppb the measurements at Verzago are in good agreement with data recently published by DAS ET AL. (2003). They measured over a maize field in North Carolina and obtained averaged methanol mixing ratios of 16.4 and 11.0 ppb in 0.5 and 2.5 m height above the tops of the plants, respectively. No spikes were reported like in our measurements. This might be partly due to the low time resolution as hourly integrated air samples were collected. WARNEKE ET AL. (2002) measured approximately 2 m above an alfalfa
field highly time resolved methanol mixing ratios between 10 and 50 ppb with some peaks up to 100 ppb. Both of these studies observed the highest methanol emissions during the day or after cutting the grass in accordance with laboratory studies. In contrast to that, our results show exceedingly enhanced mixing ratios in the late night.

Only measurements with sweet gum saplings in Alabama also revealed enhanced predawn methanol emissions (MacDonald & Fall, 1993). Explanations of the responsible processes are still speculative. MacDonald & Fall (1993) proposed a combination of improved nighttime leaf water status influencing the cell expansion rate, a methanol enrichment in the condensed water on the plant surface or a methanol accumulation inside the plant due to a reduced stomatal conductance. Holzinger et al. (2001) observed increased methanol concentrations after rainfall in a semi-rural environment in Austria and related this effect to the process already reported by Warneke et al. (1999).

At Verzago, the methanol levels are most probably of local origin as suggested by Figure 5.11. Elevated methanol mixing ratios appeared with low wind speed and relative humidities higher than 95%. Therefore, the methanol bursts might be ascribed to a condensation process and a similar process as reported by Warneke et al. (1999) and MacDonald & Fall (1993). Our findings show other characteristics than those reported by Holzinger et al. (2001). They observed decreased mixing ratios after condensation and interpreted it as an enhanced methanol removal due to wet deposition on dew-wetted surfaces. We suppose that the condensed water could dissolve the methanol on the plant surface and release it afterwards in the atmosphere. The low wind speeds possibly promotes the ac-

\[ \text{Figure 5.10: 10-day time series of methanol measured with PTR-MS in summer 2002.} \]
cumulation in the vicinity of the sampling site as it favors the condensation due to reduced vertical and horizontal mixing. A small part of the field was cut at the beginning of the campaign (mid to end of July) to enable an undisturbed light path from the DOAS instruments to the reflector, but the peaks appeared several weeks after the cut. Therefore a direct effect of the cut can be excluded and only an effect due to fermentation of the cut corn could be conceivable.

5.4 Conclusions

Three measurement campaigns within a period of 5 years were performed in the Po Basin in early summer 1998, summer 2002, and autumn 2003. Bimodal diurnal isoprene cycles were observed at the semi-rural site during each campaign and were qualitatively reproduced by a 3-dimensional Eulerian model which cannot account for local phenomena at the sampling site. The bimodal structure was most pronounced during fair weather periods due to enhanced isoprene emissions. Time series of methyl vinyl ketone (MVK) + methacrolein (MACR) showed rising concentrations shortly after the isoprene morning peak and supported the interpretation of the photochemical influence that was at least partly responsible for the isoprene decay during noontime. The second isoprene peak in the late afternoon was not followed by an increase of MVK + MACR that would be expected if the isoprene + OH reaction was the dominant process of the nighttime isoprene decay. Further analyses revealed that the reaction with NO₃ seemed to be most likely the dominating process for the nighttime isoprene decay whereas dynamic processes
i.e. advection of air masses and vertical dispersion seemed to be more important for the decay of the isoprene oxidation products.

Considerable methanol peaks were observed at the semi-rural sampling site during several nights at the end of August 2002. In contrast to most of the previous publications that reported methanol emissions driven by temperature, light, stomatal conductance, or due to cutting, the enhanced methanol levels at Verzago were found during the night with low wind speed and high relative humidities. Condensation processes either on the plant surfaces or inside the plant and/or a fermentation of cut corn close to the sampling site that was promoted under humid conditions might be responsible for the high methanol mixing ratios measured in the late night. Low wind speed could favor the enhanced levels due to reduced mixing and due to more favorable conditions for high humidities.

The interpretation of the VOC patterns at Verzago in this and the companion paper (STEINBACHER ET AL., 2004) forms an important basis and provides knowledge for the further interpretation of formaldehyde as an intermediate of the VOC oxidation in the boundary layer.

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References


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Chapter 6

Nocturnal Trans-Alpine Transport of Ozone and its Effects on Air Quality on the Swiss Plateau

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Abstract Trace gas measurements in the Leventina valley in southern Switzerland were performed in August and September 2001. Highest concentrations of secondary air pollutants (ozone and formaldehyde) were measured at an elevated site during nights with southerly winds. The analysis of ozone data at an elevated site in southern Switzerland from 1991 to 1998 corroborated that enhanced pollutant levels originating from the residual layer of the Po Basin led to an increase of ozone during spring and summer nocturnal southerly advection. Average differences of up to more than 20 ppb were found when comparing the nighttime ozone mixing ratios during persistent southerly and northerly advection. The impact of the nocturnal trans-Alpine transport on the residual layer north of the Alps could be shown by means of a case study and an analysis of a perennial time series of ozone for an elevated station north of the Alpine crest. The afternoon spring and summer ozone concentrations in the boundary layer north of the Alps were on average 2.5 ppb higher after persistent southerly advection and fair weather conditions in the previous night. This concentration increase due to nocturnal trans-Alpine transport was estimated to be responsible for additional 5% of hours with ozone levels above the Swiss national air quality standard.

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6.1 Introduction

Ozone (O$_3$) concentrations in the lower troposphere strongly increased within the last century. O$_3$ levels more than doubled in rural areas since the end of the 19th century as shown by a reanalysis of an O$_3$ time series of Montsouris, near Paris (VOLZ & KLEY, 1988). O$_3$ is an important air quality issue due to adverse health effects on humans (BRUNEKREEF & HOLGATE, 2002) and plants (FUHRER ET AL., 1997). Furthermore, O$_3$ acts as a strong greenhouse gas in the free troposphere (IPCC, 2001). O$_3$ is a secondary pollutant that is produced during the atmospheric photooxidation of volatile organic compounds (VOCs) under the presence of nitrogen oxides. The increase of O$_3$ is related to increasing emissions of the precursors associated with local and regional photochemistry as well as to an increase of the so called 'background ozone' that is influenced by large-scale photochemistry, large-scale transport, and stratosphere-troposphere exchange. A review of the tropospheric oxidation chemistry was given for example by ATKINSON (2000) and JENKIN & CLEMITSHAW (2000).

For Switzerland, STAEHELIN ET AL. (1994) compared O$_3$ measurements at an elevated site in Arosa from the 1950s and 1989 to 1991 and found a rise of O$_3$ by a factor of approximately 2.2. A time series analysis for several measurement sites in Switzerland for the 1990s revealed a slight but significant increase of the mean O$_3$ concentrations of 0.5 - 0.9 ppb yr$^{-1}$ (BRÖNNIMANN ET AL., 2002) reflecting nearly stagnant ozone levels despite of the considerable decrease of the NO$_x$ and VOC emissions in Switzerland within the last 15 years.

Until now, only a small number of publications dealt with the transport of O$_3$ and other air pollutants across the Alps. Most of them were related to foehn events i.e. to periods with strong down-slope winds that induce rising temperatures and low relative humidities on the lee side of a mountain range (WHITEMAN, 2000). The transport of atmospheric trace gases was investigated in the Alps at the Jungfraujoch (3580 m asl) by FORRER ET AL. (2000) and ZELLWEGER ET AL. (2000). A back trajectory analysis of foehn events revealed that air masses arrived at the Jungfraujoch which passed the boundary layer or the residual layer above the Po Basin (FORRER ET AL., 2000). In general, they observed a slight O$_3$ increase during south foehn events in summer. BAUMANN ET AL. (2001) performed a study dealing with the influence of south foehn on the O$_3$ concentrations in the Alpine Rhine valley. The analysis of the case study in October 1999 showed air that originated from the lower troposphere above the Po Basin in the Rhine valley south of the Lake Constance. Another study dealing with O$_3$ and the transport above the eastern part of the Alps during foehn events was performed by SEIBERT ET AL. (2000). They showed for a case study in May 1997 by means of three-dimensional back trajectories that boundary layer air from the Po Basin arrived at Innsbruck during a foehn event. A climatological study of a three-year data set showed for all observed stations enhanced O$_3$ concentrations during these episodes.
The impact was more distinct at valley stations than at the elevated sites. This can be explained by higher wind speeds that usually prevail during foehn events. Due to that, the sink mechanisms of \( O_3 \) (titration of \( O_3 \) by NO and deposition) have a weaker effect on the \( O_3 \) concentrations near the ground and \( O_3 \) remained high even during the night. **Carnuth et al.** (2002) observed a distinct \( O_3 \) increase after sunset in southern Germany by means of lidar measurements. They detected an increase by about 40% and attributed this rise supported by a backward trajectory analysis to trans-Alpine \( O_3 \) transport. Pollutants from the Po Basin were probably sucked into the Alpine valleys during the day, were lifted there to elevated layers, and were transported to the measurements site at the northern edge of the Alps. **Weber & Prévôt** (2002) performed a 10-year climatology of north foehn events and their impact on \( O_3 \) concentrations. They only considered the daily \( O_3 \) maxima and obtained strongly reduced \( O_3 \) levels in southern Switzerland at the border of the Po Basin during north foehn events in summer whereas a slight increase was detected in winter.

The Milan area and the Po Basin are densely populated and highly industrialized regions that are characterized by anthropogenic pollutants and \( O_3 \) values that are among the highest in whole Europe (**Prévôt et al.**, 1997; **Dommen et al.**, 2002). Due to the topography, a thermally induced wind system often develops during the summer that advects air from the Po Basin towards the Alps and transports the polluted air masses northwards to southern Switzerland (**Staffelbach et al.**, 1997; **Prévôt et al.**, 1997). In this paper we present selected results of such events from the CHAPOP (**Characterization of High Alpine Pollution Plumes**) field campaign in southern Switzerland in summer 2001. The findings are further supported by an analysis of a perennial time series of another measurement site in southern Switzerland. On the basis of a case study, we discuss the possible impact of an overflow of air originating from the residual layer above the Po Basin across the Alps on the \( O_3 \) levels in the northern reservoir layer. An 11-year climatology for an elevated station north of the Alpine crest generalizes this result. In contrast to the studies mentioned above, our work is not restricted to foehn events but considers all periods with nocturnal southerly advection. Finally an estimation of the implication of the trans-Alpine transport for the air quality on the Swiss Plateau is given.

### 6.2 Measurement sites

Six surface stations were operated in the Leventina valley in southern Switzerland in August and September 2001 within the scope of the CHAPOP field campaign. The main objective of the campaign was to evaluate the importance of vertical export of boundary layer air by thermal wind systems into the lower free troposphere above an Alpine valley and the impact of this process for a larger regional area (**Henne**
In this work, trace gas and meteorological data from the ground stations Dalpe and Monte Matro are presented.

*Dalpe* (1240 m above sea level (asl), 46° 28' N, 8° 47' E) is located in a rural environment in the Leventina valley, approximately 500 m above the valley ground where one of the major trans-Alpine traffic routes passes by.

*Monte Matro* (2170 m asl, 46° 24' N, 8° 55' E) is located approximately 15 km southeast of Dalpe and is situated on the north-eastern crest of the Leventina valley, around 1800 m above the valley ground. Long term measurements of wind and temperature at this site within the scope of the supplementary network (ENET) operated by MeteoSwiss were also available.

For the climatological study the following monitoring stations were used (see Figure 6.1):

*Cimetta* (1672 m asl, 46° 12' N, 8° 48' E) is an elevated measurement site in the southern Alps roughly 40 km north of the Po Basin and approximately 80 km north of Milan. Cimetta belongs to the meteorological network of automatic stations (ANETZ) of MeteoSwiss. Hourly averages were available from 1990 to 2001. Ozone and nitrogen dioxide mixing ratios were measured by the Office for Air Pollution Control of the canton Ticino. One hour mean values were available from November 1990 to December 1998.
6.3. Results and discussion

Rigi-Seebodenalp (1030 m asl, 47° 04' N, 8° 28' E) is situated in an elevated rural environment 600 m above Lake Lucerne. The station is a measurement site of the Swiss National Air Pollution Monitoring Network (NABEL). Hourly averages of NO₂, NO, O₃, CO, SO₂, and meteorological parameters from June 1991 to end of 2001 were considered for the analysis. The sampling site is located close to a north-westerly exposed slope that can induce a south-easterly down-slope wind between sunset and sunrise.

Taenikon (540 m asl, 47°28' N, 8°54' E) is a rural NABEL measurement site in the eastern part of the Swiss Plateau north of the Alps and is representative for the boundary layer of the Swiss Plateau. Hourly averages of the same parameters as for the Rigi site (except of CO) were available for 1990 to 2001.

At Guetsch (2287 m asl, 46°39' N, 8°37 E) an automatic weather station of the ANETZ network is operated. It is located close to the Gotthard Pass on the main Alpine crest, which connects the Leventina in the South with the Reuss Valley in the North. The wind direction at Guetsch is a good measure for the main air flow crossing the Alps.

O₃ was measured by UV absorption (Environics, MonitorLabs). Formaldehyde concentrations were obtained by the Hantzsch fluorescent method (Kelly & Fortuné, 1994) with commercial instruments from AeroLaser.

6.3 Results and discussion

6.3.1 Ozone and formaldehyde levels during the CHAPOP campaign

Figure 6.2 and 6.3 show time series of ozone (O₃) and formaldehyde (HCHO) at Monte Matro and Dalpe measured during the CHAPOP field campaign. At the beginning of the shown period, the Alpine region was influenced by an anticyclone associated with a ridge stretched from the Iberian Peninsula towards Germany resulting in sunny conditions and high temperatures. Weakening of the anticyclone led to a S-E oriented flow and to a north foehn event in the afternoon of August 27. Thereafter, temperatures increased even more (up to 26 °C at Dalpe and up to 18 °C at Matro) and solar radiation was still intense until a cold front passed the Alps in the morning of August 30 that resulted in overcast conditions and a temperature drop of about 9 °C at Monte Matro within 12 hours.

Within this period of 8 days, nocturnal peaks (marked with arrows in Figure 6.2) of O₃ were detected during 3 nights at Monte Matro whereas only small nocturnal peaks were observed at Dalpe. A similar phenomena of nocturnal O₃ peaks at an elevated measurement site was already observed during the VOTALP campaign at the San Bernardino Pass in summer 1996 (Furger et al., 2000; Prévôt et al., 2000b). There, approximately 23 km north-east of Monte Matro at the end of the
Mesolcina valley, an increase of $O_3$ after sunset was observed six times within a period of one month. All these events at the San Bernardino Pass were associated with southerly advection of air masses.

The time series of HCHO (Figure 6.3) shows a similar pattern with considerably increased HCHO levels during the night that came along with the $O_3$ peaks occurring at Monte Matro. Again, no comparable behavior was noticed at Dalpe. HCHO is predominantly a secondary pollutant that is produced by the atmospheric oxidation of a large variety of VOCs. Primary emissions account just for a small

![Figure 6.2: Ozone mixing ratios at Monte Matro and Dalpe for an 8-day period in 2001. The arrows denote events with increased nocturnal ozone and formaldehyde mixing ratios at Monte Matro.](image)

![Figure 6.3: Same as Figure 6.2 but for formaldehyde.](image)
6.3. Results and discussion

Figure 6.4: Ozone mixing ratio, meridional wind, and water vapor mass mixing ratio at Monte Matro in summer 2001.

amount of the atmospheric HCHO loading (FRIEDFELD ET AL., 2002). Primarily emitted anthropogenic pollutants showed usually no considerable increase at Monte Matro during these nights. Therefore, we conclude that an aged air mass reached the measurement site during these events. The nocturnal increase of the O₃ concentrations at Monte Matro was associated with air masses coming from the south of the measurement site. This is also corroborated by radio soundings made close to Faido in the Leventina valley approximately 10 km northwest of Monte Matro in the night from August 26 to 27 (not shown here). These results confirmed that the increase of O₃ and HCHO during this night matched with southerly wind in 2 to 3 km height asl whereas northerly winds prevailed within the lowest parts of the valley. Figure 6.4 shows a longer time series of O₃ mixing ratios, the meridional component of the wind speed, and the water vapor mass mixing ratio at Monte Matro. High O₃ concentrations were linked with southerly winds and enhanced humidity. All these factors point to an advection of usually more humid and O₃-rich boundary layer air from the Po Basin. An influence of stratospheric or upper tropospheric air is unlikely because these air masses are expected to have low water contents.

The fact that the highest O₃ and HCHO mixing ratios were found during the night indicate that the up-valley wind that developed usually during the day was not strong enough to advect the most polluted air masses all the way from the Po Basin to the Monte Matro. Neither HCHO nor O₃ is considerably produced during the night. Therefore, the peak levels of the pollutants only reached Monte Matro if southerly winds prevailed at the altitude of Monte Matro even after the daily
thermally induced up-valley breeze had ceased.

SANDRONI ET AL. (1994) analyzed O₃ measurements in the south-western and eastern Alpine regions from 1987 to 1991 and mentioned that the photochemical activity at the bottom of the valley influences the O₃ concentrations in the higher altitudes only up to about 1800 m asl. But the situation at Monte Matro can be different due to effective mixing of air masses by thermal airflow in the complex terrain of the Alpine foothills south of Monte Matro. BONASONI ET AL. (2000) postulated the formation of nighttime reservoir layers when discussing high nocturnal O₃ values at Monte Cimone (2165 m asl) in the Italian Northern Apennines. These layers in which high O₃ mixing ratios can be reached are due to high mixing heights above the Po Basin. This possibility is supported by another study dealing with the transport of boundary layer air from the Po Basin to high-Alpine sites (SEIBERT ET AL., 1998) that detected air masses coming from the bottom of the Po Basin to Sonnblick, Austria at 3106 m asl and to the Jungfraujoch at 3580 m asl. HENNE ET AL. (2004) showed for the deep Alpine valleys Mesolcina and Leventina that these kind of valleys can act as effective 'air pumps' to inject pollutants from the boundary layer into the so called injection layer during daytime.

6.3.2 Ozone at Cimetta (1672 m asl, south of the Alpine crest)

In this section we try to generalize the findings we made during the above mentioned field campaigns. For this purpose, we chose the ozone time series measured at Cimetta in the 1990s. If the enhanced concentrations of secondary pollutants during nights with southerly advection at elevated sites in Ticino are a general phenomenon, it should be also observable in the perennial time series at Cimetta that is located slightly lower and closer to the Po Basin than Monte Matro.

Hourly O₃ values at Cimetta were classified according to the vector-averaged wind direction of the preceding 6 hours, which approximately corresponds to the transport time from the greater Milan area to the station assuming a wind speed of 2 m s⁻¹. The median O₃ mixing ratios as a function of the wind classes for different seasons and daytimes are illustrated in Figure 6.5. No considerable dependence on the wind direction was observed for winter (December, January, February; panel b) and fall (September, October, November). For all data (panel a), the difference ΔO₃ of the median between the three south sectors (112.5° to 247.5°) and the three north sectors (292.5° to 67.5°) was 11.5 ppb. A lower difference could be observed during spring (March, April, May; ΔO₃ = 7.5 ppb), whereas during summer (June, July, August; ΔO₃ = 19.5 ppb) a strong distinction between northerly and southerly advection existed. Restricting the analysis to the nighttime data (11 PM to 6 AM UTC) to focus on residual layer conditions, ΔO₃ was slightly lower for the whole data set (panel a) as well as for all summer data (panel c). The largest difference (ΔO₃ = 21.5 ppb) was obtained for the summer and nighttime
6.3. Results and discussion

Data when only fair weather conditions (mean relative humidity within the last 24 hours < 80%) were considered.

In fall and winter, non-local processes related to 'background ozone' like large-scale photochemistry, large-scale transport, and stratosphere-troposphere exchange.

![Diagram](image)

Figure 6.5: Relation of the median ozone mixing ratios and the wind direction at Cimetta for different seasons and daytimes. Each wind category represents a wind sector of 45°. The differences ($\Delta O_3$) between the median ozone mixing ratio of the 3 northern sectors (292.5 to 67.5°) and the 3 southern sectors (112.5 to 247.5°) are (a) 11.5 ppb (all data), 10.0 ppb (nighttime), (b) -2.0 ppb (winter), 7.5 ppb (spring), 19.5 ppb (summer), 4.0 ppb (fall), (c) 18.5 ppb (summer, night), 21.5 ppb (summer, night, fair). The wind direction calculation was based on 6h-averages of the wind components. Fair weather conditions are defined by a 24h-average of the relative humidity < 80%. Note that the origin of the plots do not correspond to zero ppb.
dominate the O₃ levels. Therefore, no dependence on the local wind direction was observed. In summer the local photochemistry becomes the dominant factor. High solar radiation leads to more efficient photochemical activity and causes an enhanced oxidation of the O₃ precursors. The solar radiation also results in a more efficient vertical transport. Therefore, locally emitted and locally produced trace gases can be carried to the measurement site by convection. Moreover, high mixing heights can form nighttime reservoir layers at upper levels that include high O₃ concentrations especially above the Po Basin. The enhanced photochemistry and the convection became visible in the distinct difference for southerly and northerly advection in summer considering the whole day (see Figure 6.5b). The pronounced dependence on the wind direction in the night (see Figure 6.5c) is related to differences of the trace gas concentration levels of the nighttime reservoir layer. The ΔO₃ during the night is similar to the difference during the whole day because the residual layer reflects an elevated remaining portion of the daytime boundary layer. During fair weather conditions the photochemistry, the convection, and therefore the reservoir layer were even more developed and the effect got more distinct (see Figure 6.5c).

Enhanced O₃ concentrations were observed during southerly advection in spring. Several studies already reported high tropospheric O₃ concentrations in spring especially at elevated sites (Bonasoni et al., 2000; Brönnimann, 1999; Brönnimann et al., 2001; Monks, 2000). Brönnimann (1999) and Brönnimann et al. (2001) analyzed early spring O₃ episodes in Switzerland and related the increased O₃ values to several reasons: the rapidly increasing solar radiation that changes the chemical conditions, enhances the regional photochemistry, and accelerates the oxidation of at least partly accumulated VOCs, the advection of upper tropospheric and stratospheric air, and the advection of photochemically formed O₃ from the boundary layer of more southerly countries where the solar radiation is already higher. Mean diurnal cycles of O₃ at elevated stations for fair weather days in February to April (1992 to 1997) showed a slightly enhanced occurrence of daily O₃ maxima after midnight whereas nocturnal peaks were measured very rarely in lower altitudes (Brönnimann, 1999). The author suggested that this feature was caused by O₃-rich air masses from upper layers that incorporated into the mountain flow. In our study, high O₃ mixing ratios at Cimetta during the night usually were not correlated with low humidities so that a considerable upper tropospheric or stratospheric influence is not likely.

Beside the analysis of all O₃ data, we also analyzed the daily O₃ maxima. We defined the daily O₃ maximum as the highest one-hour value between noon and noon the following day. The maxima are especially of interest in terms of the adverse effects of O₃ on human health and on plants. The spring and summer months were considered in the further analysis because the highest O₃ levels appear within these months in the boundary layer and the lower free troposphere. Figure 6.6 shows the dependence of the daily O₃ maxima on the wind direction similar to
6.3. Results and discussion

Figure 6.6: Relation of the median ozone mixing ratios and the median of the daily ozone maxima and the wind direction at Cimetta. The wind direction calculation was based on 6h-averages of the wind components. Data are restricted to spring + summer and nighttime conditions. Wind categories, fair weather conditions, and ΔO₃ are defined as in Figure 6.5. ΔO₃(hourly) = 18.5 ppb, ΔO₃(max) = 38.5 ppb. Scaling is different to Figure 6.5.

Figure 6.5. For comparison, the respective results for all O₃ data are illustrated, too. It is conspicuous that the influence of wind direction on O₃ maxima is much more pronounced than on all O₃ data. The ΔO₃ is reaching values of up to 38.5 ppb and is nearly doubled considering only the maxima compared to all data.

6.3.3 A case study of ozone transport from south to north of the Alps

In the following, we investigate if the high O₃ concentrations south of the Alps can significantly influence the O₃ concentrations north of the Alps. An interesting episode that exemplifies the interaction of the residual layer north and south of the Alps happened from April 17 to 21, 1996. Figure 6.7 shows the O₃ mixing ratios at Cimetta and Rigi as well as wind speed and wind direction at Rigi and the wind direction at Guetsch for this period. On April 17, a stable and large amplitude ridge on the 500 hPa level stretched from the Mediterranean area towards southern Sweden. It only moved slowly towards southeast and brought cloudless weather and high temperatures in Central Europe for several days. During the nights with persistent southerly wind at Rigi and Guetsch (April 19/20, April 20/21), the O₃ mixing ratios at Cimetta and Rigi were identical. Whereas during nights with very
Figure 6.7: Time series of 1-hour averages of ozone mixing ratios at Cimetta and Rigi, the wind direction at Guetsch, and the wind speed and direction at Rigi during a 5-day period in April 1996.

low wind speeds (April 18/19) or northerly flows (April 17/18) at Rigi the O₃ levels were considerably lower than at Cimetta. From April 19 to 21 the wind direction at Guetsch stayed persistently south while the wind direction at Rigi changed during the day to north illustrating the local influence of the boundary layer at the less elevated Rigi site. The wind direction at Guetsch was also linked to rather elevated O₃ levels in the early morning of April 17 despite of low wind speeds at Rigi.

6.3.4 Air flow across the Alps

Figure 6.8 presents an idealized schematic of the flow structures in the Alpine region during days with high insolation and weak synoptic pressure gradients. It illustrates that a significant advective trans-Alpine air mass exchange below the injection layer only takes place during the night. In the deep Alpine valleys of this region the katabatic winds develop during the night only in the lowest approximately 500 m above the valley floor (PRÉVÔT ET AL., 2000b) and a synoptically influenced air flow across the Alps exchanging air of the residual layers is possible. During the day the convective boundary layer usually reaches heights of about 2000 m asl in the Alpine valleys (HENNE ET AL., 2004), from which air within the valley can be injected into air masses up to 4 km asl (CARNUTH ET AL., 2002; PRÉVÔT ET AL., 2000a). The up-valley winds lead to convergences near the Alpine crest. Consequently, trans-alpine transport is restricted mostly to the free troposphere and the injection layer.
6.3. Results and discussion

6.3.5 Ozone at Rigi (1030 m asl, north of the Alpine crest)

In this section, a climatological is given to quantify the average O₃ increase at Rigi when southerly advection takes place. Only nocturnal data at Rigi was considered to restrict the analysis to periods non-influenced by boundary layer air. During the night we assume that the Rigi station is representative for the residual layer. Figure 6.9 shows the relation between the median O₃ mixing ratios and the wind direction at Rigi for spring and summer nighttime and fair weather conditions. Due to a possible local influence on the wind conditions during the night at Rigi (slope winds due to the local topography during periods with weak synoptic winds), the data of the three southernmost sectors (135° and 180° and 225°) were only considered when the wind direction at the Guetsch was between 112.5° and 247.5°. The results were not very sensitive to the inclusion/exclusion of this additional criterion (compare the second and the third column in Table 6.1) but it was taken into account to eliminate hours with southerly winds driven only by the local meteorology and
not by trans-Alpine transport. This assumption is still the main uncertainty of the following analysis. We chose an approach based on local wind measurements which involves uncertainties concerning larger scale representativeness. However, meteorological models also have problems to represent wind fields above complex terrain.

The O₃ difference for southerly and northerly advection at Rigi is considerably smaller than at Cimetta. Whereas the ΔO₃ at Cimetta reached 19.5 ppb, the O₃ difference at Rigi was only 11.0 ppb reflecting a smaller influence of the southerly advection on the O₃ levels of the residual layer north of the Alps. While the median O₃ mixing ratio for the three most southerly wind sectors during spring and summer, night, and fair weather conditions was 67.5 ppb at Cimetta, the median reached at Rigi only 53.6 ppb for the same conditions. Dilution effects and possibly dry deposition can reduce the O₃ concentration during the transport across the Alps and in many cases the highest concentrations do not get far enough north.

The O₃ difference for southerly and northerly advection illustrated in Figure 6.9 can be caused by other effects beside the advection of primary and secondary pollutants from the regions south of the Alps. Southerly advection can favor less

![Figure 6.9: Relation of the median ozone mixing ratios and the wind direction at Rigi for nighttime (11 PM to 6 AM) during spring and summer months and fair weather conditions. ΔO₃ (defined in Figure 6.5) = 11.0 ppb. For the mean wind classes from the south (90°, 135° and 180°) data only were considered when the mean wind direction at Guetsch was between 112.5° and 247.5° to exclude data with only locally southerly wind at Rigi. The wind direction calculation was based on 6h-averages of the wind components.](image-url)
6.3. Results and discussion

Table 6.1: Differences of median $O_3$ ($\Delta O_3$) and median air temperature ($\Delta T$) at Rigi for periods with south and north advection under various ambient conditions.

<table>
<thead>
<tr>
<th>conditions</th>
<th>spring &amp; summer</th>
<th>spring &amp; summer, night, fair weather</th>
<th>spring &amp; summer, night, fair weather</th>
<th>spring &amp; summer, night, fair weather</th>
</tr>
</thead>
<tbody>
<tr>
<td>difference</td>
<td>R$\uparrow$-R$\downarrow^a$</td>
<td>R$\uparrow$-R$\downarrow$</td>
<td>R$\uparrow$G$\uparrow$-R$\downarrow^b$</td>
<td>R$\uparrow$G$\uparrow$-R$_{rc}^c$</td>
</tr>
<tr>
<td>$\Delta O_3$ [ppb]</td>
<td>15.5</td>
<td>10.8</td>
<td>11.0</td>
<td>4.5</td>
</tr>
<tr>
<td>$\Delta T$ [°C]</td>
<td>4.9</td>
<td>2.7</td>
<td>2.9</td>
<td>1.8</td>
</tr>
</tbody>
</table>

$^a$ R$\uparrow$: 6h-mean wind direction at Rigi between 112.5 and 247.5°. R$\downarrow$: 6h-mean wind direction at Rigi between 292.5 and 67.5°

$^b$ R$\uparrow$G$\uparrow$: 6h-mean wind direction at Rigi between 112.5 and 247.5° and 6h-mean wind direction at Guetsch between 112.5 and 247.5°

$^c$ R$_{rc}$: Rigi residual; all conditions except of R$\uparrow$G$\uparrow$

cloudy conditions on the lee side of the mountains or a higher temperature regime. The Rigi data shows an increase of $O_3$ with increasing temperature by about 1 ppb per 1 °C for spring and summer nighttime and fair weather. An analysis of the median air temperatures of the three southernmost to the three northernmost wind sectors analogous to the $\Delta O_3$ calculation resulted in a $\Delta T$ of 2.9 °C indicating that at least a part of the $O_3$ differences can be related to an air temperature bias. The wind speed was not enhanced during southerly advection so that a different intensity of dry deposition is expected to be irrelevant. The different meteorological situations (e.g. less cloudy and drier conditions) are already considered roughly by the selection of fair weather days.

Table 6.1 summarizes the differences of the median $O_3$ values for southerly and northerly advection for different conditions. An $O_3$ difference of 15.5 ppb and a temperature difference of 4.9 °C were found when considering all spring and summer nighttime data whereas only 10.8 ppb and 2.7 °C remained with the restriction to fair weather days. This reflects the influence of the different synoptic conditions and confirms that southerly advection favors generally an attenuation of the cloud cover due to the subsidence and a drying of the air masses. When only cases with southerly advection at Guetsch and at Rigi (between 112.5° and 247.5° (R$\uparrow$G$\uparrow$)) were considered, the $O_3$ and temperature difference increased slightly. Comparing the R$\uparrow$G$\uparrow$ cases with all the other data (Rigi residual data), the $\Delta O_3$ and $\Delta T$ were reduced to 4.5 ppb and 1.8 °C. The Rigi residual data also comprised cases with local southerly advection at Rigi but with a prevailing non-southerly wind at Guetsch. The local influence of the down-slope winds at Rigi mainly becomes important during meteorological conditions with weak synoptic winds. These situations appear preferably during anticyclonic situations that also favor open sky
6.3.6 Implications for the Swiss Plateau north of the Alps

The nocturnal \( \text{O}_3 \) values in the residual layer are usually the initial conditions for the \( \text{O}_3 \) concentration of the next day. Neu et al. (1994) showed by means of \( \text{O}_3 \) soundings made on the Swiss Plateau that the \( \text{O}_3 \) mixed down from the residual layer contributed 50 to 70\% to the maximum concentration near the surface on the following day. Therefore, the advection from south of the Alps does not only influence the residual layer north of the Alps but also possibly the \( \text{O}_3 \) concentration in the whole mixed boundary layer of the next day.

The Swiss Plateau is located between the Jura in the northwest and the Alps in the southeast (see Figure 6.1). The area is the most densely populated and industrialized area in Switzerland where the \( \text{O}_3 \) levels exceed regularly the Swiss national air quality standard of 120 \( \mu \text{g m}^{-3} \) (about 60 ppb; one-hour average not to be exceeded more than once per year) during summer smog episodes (Wanner et al., 1993; Dommen et al., 1995). The data series of Taenikon, a rural station with moderate anthropogenic influence located in the east of the Swiss Plateau was investigated. We selected spring and summer nighttime data with fair weather conditions and southerly nocturnal advection at Rigi and analyzed the \( \text{O}_3 \) levels at Taenikon 12 hours later. Other than in the previous section, the nighttime was restricted to 1 to 6 AM because only afternoon (1 to 6 PM) \( \text{O}_3 \) mixing ratios at Taenikon were included in the analysis when photochemical \( \text{O}_3 \) formation is dominant and usually the highest \( \text{O}_3 \) concentrations appear. Comparing the cases with southerly wind at Rigi and Guetsch with all other cases (in analogy to the rightmost column in Table 6.1), an \( \text{O}_3 \) difference of 5.0 ppb (\( \Delta \text{T} = 2.2 \, ^{\circ}\text{C} \)) at Rigi occurred. The slight difference to Table 6.1 arose from the different selection of nighttime hours. The analysis of the corresponding \( \text{O}_3 \) and temperature data 12 hrs later at Taenikon (approximately 50 km north of Rigi) showed that also at Taenikon a significant increase of \( \Delta \text{O}_3 \) of 2.5 ppb (\( \Delta \text{T} \) of 0.8 \( ^{\circ}\text{C} \)) could be detected. These differences are significant at a level of more than 99.9\% (two-population (independent) \( t \)-test). The median wind speeds for the different selections differed just slightly and could cause only a negligible effect. This reflects that a signal of nocturnal transalpine transport from the south is detectable in the \( \text{O}_3 \) time series in the boundary layer on the Swiss Plateau.

In the following, it is investigated if and to what extent this 2.5 ppb enhancement caused by the southerly advection could increase the number of hours with hourly mean \( \text{O}_3 \) mixing ratios above the Swiss national air quality standard of 120 \( \mu \text{g m}^{-3} \) at Taenikon. Again, we took the spring and summer nighttime (1 to 6 AM) data with fair weather for conditions with southerly and non-southerly advection at Rigi and Guetsch and counted the hours with \( \text{O}_3 \) mixing ratios above 60 ppb at Taenikon 12 hrs later. The percentage difference of exceedance hours between the
two samples, weighted by sample size, implies that nocturnal southerly advection could be responsible for additional 5% (116 hrs for the whole investigated period of $10\frac{1}{2}$ years) of exceedances. The estimation holds for O$_3$ exceedances in the spring and summer afternoon during fair weather conditions. The selection of spring and summer months with fair weather conditions covered 96% of the exceedances of the whole year with fair weather conditions. This estimation shows that a considerable amount of exceedances on the Swiss Plateau is favored by nocturnal trans-Alpine transport of primary and secondary air pollutants from Northern Italy to the northern Swiss residual layer, which is finally mixed into the boundary layer.

6.4 Conclusions

Measurements in the Leventina valley in southern Switzerland in summer 2001 showed nighttime peak concentrations of secondary pollutants like ozone and formaldehyde at mountain crests concurrent with southerly winds. This was caused by boundary layer influenced residual layer air that was transported from the Po Basin to the measurement site. Southerly advection during the night was necessary for the elevated trace gas concentrations at Monte Matro because the most polluted air masses of the Po Basin could not reach the crest within a daytime thermal up-valley wind period. The good correlation of the O$_3$ level at Monte Matro with the H$_2$O content illustrated the contribution of boundary layer air to the enhanced trace gas levels.

The analysis of the perennial time series of O$_3$ at the elevated measurement site Cimetra corroborated the findings at Monte Matro and revealed considerably enhanced O$_3$ levels during southerly advection for spring and summer. The analysis restricted to nighttime data under residual layer conditions showed similar signals in the O$_3$ differences for southerly and northerly advection. The difference of the medians of the daily O$_3$ maxima between southerly and northerly advection yielded 38.5 ppb for spring and summer nighttime data and fair weather conditions.

A case study illustrated exemplarily the interaction of the residual layers north and south of the Alps with the wind data at Guetsch as a good indicator for the trans-Alpine airflow. An extended analysis including the perennial time series of meteorological and chemical data at Rigi and Guetsch generalized the findings and pointed out that the influence of southerly advection was clearly visible in the residual layer north of the Alps. Only nocturnal O$_3$ values were considered to restrict the analysis to residual layer conditions. Southerly airflow and fair weather at Guetsch and Rigi resulted in 11.0 ppb higher O$_3$ mixing ratios at Rigi compared to northerly advection. A difference of 4.5 ppb remained when periods with advection from south of the Alps with all other episodes were compared. A small fraction of this O$_3$ increase could be related to higher temperatures associated with southerly advection. At the rural station Taenikon on the Swiss Plateau
afternoon O$_3$ mixing ratios were on average 2.5 ppb higher under conditions of
advection from south of the Alps during the previous night than compared to
other wind directions.

Finally, we studied the effect of the average O$_3$ increase of 2.5 ppb on the number
of violations of the Swiss national air quality standard. We estimated an absolute
increase of hourly exceedances of 116 hrs for a period of 10 1/2 years. On average, this
results in additional 11 hrs of exceedances per year or a relative increase of 5.1% (it
should be kept in mind that the one-hour average should not to be exceeded more
than once per year). Therefore, the advection of residual layer air from the Po
Basin across the Alpine crest during the night influences primarily the nocturnal
residual layer north of the Alps. But as shown in our work, even an influence on the
afternoon air quality of the boundary layer of the densely populated Swiss Plateau
is measurable.

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Chapter 7

Final Remarks and Outlook

A Proton Transfer Reaction Mass Spectrometer (PTR-MS) was successfully tested, characterized, implemented for atmospheric trace gas measurements, and used during laboratory and field campaigns. It turned out that the novel technique is a useful tool to measure volatile organic compounds (VOCs) with a high time resolution and a low detection limit. As only the masses of the ion and not individual VOCs are determined, different isomers can not be resolved and unknown contributors to a certain mass can never be excluded. Furthermore, a fragmentation during ionization depending on the settings of the instrument can occur for certain species despite the soft ionization technique. Both effects can complicate the interpretation of the mass spectra considerably. Therefore, parallel measurements with another techniques like gas chromatography (GC) can ideally complement the PTR-MS measurements even if only data at lower time resolutions are available. Another approach couples at least periodically a gas chromatographic column with a PTR-MS (GC-PTR-MS) to separate the contributions of different VOCs to a single mass channel (WARNEKE ET AL., 2003). A different development combined the proton transfer ionization with an ion trap mass spectrometer (PRAZELLER ET AL., 2003). A higher duty cycle of ion trap mass spectrometry (ITMS) compared to a linear quadrupole allows an improvement especially for measurements where concentrations change rapidly and where full spectra are desirable. Furthermore, ITMS enables to perform MS/MS on mass selected ions. Ions of interest of specified m/z can be isolated and collisionally dissociated. Even if this technique works for the moment only in the 100 ppb range, it is still a promising technique for future applications. The conventional PTR-MS technique is also still under further development. The manufacturer has shown that the application of a third turbo molecular pump, which evacuates the area between the drift tube and the quadrupole, allows the use of bigger lenses resulting in a 2-3 times higher primary ion signal. The development of a compact PTR-MS (IONICON Analytik GmbH, Innsbruck, Austria) with lower weight, smaller dimensions and a cheaper price could even open the field of trace gas monitoring with this technique.
Reaction chamber studies using the PTR-MS showed the skills of the instrument and revealed that the monitoring of the gas phase species contributed significantly to understand the formation of secondary organic aerosol (SOA) from gaseous precursors. Polymerization reactions are an important process during the formation of SOA aerosols. Nitrous acid (HONO) measurements should be conducted to characterize better the possible effects of wall reactions and to learn more about the actual radical conditions in the reaction chamber. After the detailed study of the degradation of 1,3,5-trimethylbenzene and the subsequent SOA formation as a representant of an anthropogenically emitted VOC, further studies are conducted with $\alpha$-pinene, a VOC with only biogenic sources. A comparison between model results and measurements for the $\alpha$-pinene degradation is planned and an investigation of the polymerization reactions for $\alpha$-pinene products will be conducted. An evaporation unit is already constructed to use the PTR-MS not only for on-line measurements of trace gases but also for measurements of the organic composition of the aerosols. If the concentrations are high enough, this can be done on a real-time basis. First results from reaction chamber experiments show promising results that a pre-concentration is not necessary for these laboratory measurements. For ambient air measurements however, an accumulation on a trap with subsequent injection is most probably necessary.

Measurements of VOCs, inorganic species, and meteorological conditions were performed during several campaigns in the Po Basin. Different toluene to benzene ratios during the three campaigns enabled an identification of a 'weekend effect' as well as a 'vacation effect' when anthropogenic emissions were lower due to less traffic and reduced industrial activities, respectively. Bimodal diurnal cycles of isoprene with highest concentrations in the morning and the evening were measured that could be explained by an interaction of emissions, vertical mixing, and chemistry. The main objective of the campaigns in 2002 and 2003 was the improvement of the knowledge of the regional distribution of formaldehyde (HCHO) in the Po Basin as well as the role of different VOCs producing HCHO and the role of HCHO as an intermediate of the VOC oxidation in the boundary layer. The detailed analysis of the characteristic VOC patterns will act as a good basis for future studies within this international project. The further focus of the Laboratory of Atmospheric Chemistry will be on an assessment of the primary and secondary anthropogenic emission fractions of HCHO in the Po Basin and on the role of HCHO in the context of the measured VOC/O$_3$/NO$_x$ concentrations using aircraft measurements and ground-based data from Verzago.

The transport of O$_3$ from the Po Basin to the north of the Alps was investigated climatologically since two field campaigns in the summer 1996 and 2001 showed a recurrent feature with highest O$_3$ concentrations at the San Bernardino (1996) and with elevated O$_3$ and HCHO levels at the Monte Matro (2001) during nights.
with southerly advection. The analysis of a perennial time series at Cimetta corroborated the findings. The inclusion of O₃ data at Rigi showed a significant but less distinct effect even for the residual layer north of the Alps. The impact of the nocturnal trans-Alpine transport of O₃ for the boundary layer north of the Alps was investigated using an O₃ time series at Taenikon and an increase of air quality violations was found. An expanded analysis using other stations with perennial time series could be performed in the future to confirm the results from this study. In addition, model simulations or trajectory calculations could be useful tools to improve the understanding of the air flow across the Alps in terms of the transport of air pollutants, which requires future development because the respective processes are not well resolved in present models.

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List of Publications


149

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