Characterization of NO\textsubscript{x} Sources based on Tracer Correlations in Innsbruck

MASTER'S THESIS

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Abstract

In Europe, traffic is one of the largest emitters of Nitrogen Oxides (NO\textsubscript{x}), and therefore plays a significant role for air pollution (European Commission 2016). The European Commission (2017) assessed that air pollution is killing up to 3 times more people in Europe – indirectly by long-term-consequences – than by traffic accidents. Air quality management is thus an important legislative instrument used since the 1970s to improve air quality across the European continent. Different regulative strategies, like the Gothenburg protocol, have been implemented for the last decades in order to improve air quality standards and reduce emission levels from automobiles (European Environmental Agency 2013). Despite these efforts, the reduction of observed concentration changes is often not as large as projected (Vaughan et al. 2015).

Innsbruck, an inner-alpine city situated along the Brenner motorway, which is one of the busiest N-S corridors across the alps for the transport of goods, has been exceeding annual NO\textsubscript{2} limits since 2004 (Weber et al. 2016). Already Gorai et al. (2015) has noticed the problematic of local meteorology on concentrations why the special location in a valley, surrounded by mountains up to 2000m, also represents a challenging task for the interpretation of NO\textsubscript{x} concentration trends that is characterized by dominant wind systems such as valley up and down wind, slope winds and Foehn. Despite these challenges, classic concentration measurements have been conducted since decades and have been used to evaluate concentration trends over the years (Egger et al. 2017). In this thesis, a new approach (the turbulent enhancement ratio method) was tested in order to improve the interpretation of local NO\textsubscript{x} concentrations in an urban area, surrounded by mountains with daily dominant wind systems. In addition, this thesis evaluates whether the approach should help to improve the quantification of NO\textsubscript{x} sources within a well-defined footprint in the inner-city of Innsbruck.
The turbulent enhancement ratio method is based on enhancement ratios, which are often used to quantify trace gas emission ratios for single plumes (e.g. isolated point sources). To make this approach applicable in a completely different situation it was adopted and modified. The most important modification was the change from low frequency measurements to high frequency measurements which allowed recording turbulent structures of the lower atmosphere.

The turbulent enhancement ratio method was applied to NO\textsubscript{x} and CO\textsubscript{2} data and showed comparable results to other methods like the direct Eddy-Covariance method. A daily course of NO\textsubscript{x} over CO\textsubscript{2} enhancement ratios is affected by two dominant combustion sources. Traffic load and domestic fuel use are varying over the day and can describe more than 90% of the variations. A pronounced weekend to weekday variation of NO\textsubscript{x}/CO\textsubscript{2} enhancement ratios confirms traffic as an important NO\textsubscript{x} source. It can be concluded that the turbulent enhancement ratio method can be used to assess urban emission sources. Measurements confirm the importance of traffic and domestic fuel as dominant NO\textsubscript{x} sources in the inner-city of Innsbruck.
Acronyms

ACINN Institute of Atmospheric and Cryospheric Sciences
CH Hydrocarbon (radical)
CL Chemiluminescence
CO Carbon Monoxide
CO₂ Carbon Dioxide
DU Detector Unit
EEA European Environmental Agency
FM Flow Meter
f-NO primary Nitric Oxide
f-NO₂ primary Nitrogen Dioxide
EnR Enhancement Ratio
FR Flux Ratio
HC Hydrocarbon
HCN Hydrogen Cyanide
HDV Heavy Duty Vehicle
HO₂ Hydroperoxyl (radical)
H₂O Hydrogen Oxide (water)
iNNAQS iNnsbruck Air Quality Study
LDV Light Duty Vehicle
Mo Molybdenum
MoO₂ Molybdenum(IV) Oxide (Molybdenum Dioxide)
MoO₃ Molybdenum Trioxide (Molybdenum(VI) Oxide)
MRC Main Reaction Chamber
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>NaN</td>
<td>Not a Number</td>
</tr>
<tr>
<td>NCO</td>
<td>Cyanate</td>
</tr>
<tr>
<td>NMVOC</td>
<td>Non-Methane Volatile Organic Compounds</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>NO</td>
<td>Nitric Oxide</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>Nitrogen Dioxide</td>
</tr>
<tr>
<td>NO$_2^*$</td>
<td>Excited Nitrogen Dioxide</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>Nitrogen Oxides</td>
</tr>
<tr>
<td>MRC</td>
<td>Main Reaction Chamber</td>
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<tr>
<td>O</td>
<td>Oxygen</td>
</tr>
<tr>
<td>O$_2$</td>
<td>Molecular Oxygen</td>
</tr>
<tr>
<td>O$_3$</td>
<td>Ozone</td>
</tr>
<tr>
<td>OG</td>
<td>Ozone Generator</td>
</tr>
<tr>
<td>OH</td>
<td>Hydroxyl (radical)</td>
</tr>
<tr>
<td>PAN</td>
<td>Peroxyacetyl Nitrate</td>
</tr>
<tr>
<td>PFA</td>
<td>Perfluoralkoxy-Polymere</td>
</tr>
<tr>
<td>PBL</td>
<td>Planetary Boundary Layer</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate Matter</td>
</tr>
<tr>
<td>PMT</td>
<td>Photo Multiplier Tube</td>
</tr>
<tr>
<td>QAQC</td>
<td>Quality Assurance and Quality Check</td>
</tr>
<tr>
<td>RO$_2$</td>
<td>Peroxy Radical</td>
</tr>
<tr>
<td>SEDM</td>
<td>Silent Electrical Discharge Method</td>
</tr>
<tr>
<td>TER</td>
<td>Turbulent Enhancement Ratio</td>
</tr>
<tr>
<td>TKE</td>
<td>Turbulent Kinetic Energy</td>
</tr>
<tr>
<td>UBL</td>
<td>Urban Boundary Layer</td>
</tr>
<tr>
<td>UCL</td>
<td>Urban Canopy Layer</td>
</tr>
<tr>
<td>UIBK</td>
<td>University of Innsbruck</td>
</tr>
<tr>
<td>US EPA</td>
<td>United States Environmental Protecting Agency</td>
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Chapter 1

1 Introduction

The first chapter is focusing on the motivation and provides background information on the thesis topic. Additionally, the theory of the planetary boundary layer (PBL) and turbulence used in subsequent chapters is provided in more detail. Finally, the goals and outline of the thesis is defined at the end of this chapter.

1.1 Motivation

Nitric oxide (NO) and nitrogen dioxide (NO₂) – often better known as nitrogen oxides (NOₓ) – are, among other things, the result of processes of combustion (with oxygen). Especially NO₂ is known to be harmful for human health and ecosystems (Schindlbacher et al. 2013). In 2011 47% of total NOₓ emissions in Europe is directly related to road transport what makes it the most important source of the trace gas (Guerreiro et al. 2014). In agreement with the national states the European Union has introduced the Gothenburg protocol to continuously reduce NOₓ concentrations in 1999. This has led to a 48% decrease of total NOₓ between 1990-2011 (Schindlbacher et al. 2013). According to Schindlbacher et al. (2013) technological improvement in road transport in combination with regularly introduction of new EU emission standards for all engine types hassled to that emission reduction despite continuously increasing traffic activities during the same time period. However, trends of NO₂ concentration differ from trends in NOₓ. While NOₓ has decreased by 27% in the urban background atmosphere between 2002 to 2011, NO₂ only decreased by 8% (Guerreiro et al. 2014). Beevers et al. (2012) showed that the reason is associated with diesel driven cars
that have a higher NO₂/NOₓ emission ratio. This development is problematic because NO₂ is regarded to be more harmful for human health than NO (Sharma 1994). In 2011 86% of all European NO₂ exceedance occurred at traffic measurement stations (Guerreiro et al. 2014). Guerreiro et al. (2014) calculated that around 20% of the Europeans are affected by this NO₂ exceedance. In Austria, similar observations were made in 2015. 22 of 144 NO₂ and NOₓ measurement stations exceeded the annual limits. All of these were situated in urban areas or along motorways. The highest averaged annual concentrations were observed in Vomp A12, Salzburg Rudolfsplatz, Hallein A10 and in Vienna Hietzinger Kai (Spangl and Nagl 2016). In general, inner alpine cities are more affected by pollution due to a reduced air volume and a slower air exchange with the Alpine foreland influencing concentration levels of pollutant gases. Innsbruck, like many urban centres, is particularly impacted by high traffic loads due to commuter traffic from the surrounding region.

Figure 1.1: NO₂ concentration levels and their regulatory limits: Since 2004, the annual NO₂ limit has been exceeded at the Fallmerayerstreet in Innsbruck. 1) annual mean value. 2) daily mean value. 3) half-hour average value (data taken from Land Tirol - Verkehrsbericht Tirol (1999 – 2015) and visualized by the author)

In addition, the Brenner motorway is situated along the southern part of the city. The Brenner axis is the most used corridor for transport of goods across the Alps. Since 1980s the traffic volume in Tyrol increased by more than 200% (Allinger-Csollich et al. 2016) and this resulted in a continuous increase of air pollution in the Inn valley before
introducing air quality management. Hence, the Tyrolian government started with regulative measures in the early 90s to improve air quality for the local population. Nevertheless, the statutory limits are regularly exceeded, also for example, at an air quality station (Fallmerayerstreet), which is situated near the field site, that this thesis is focusing on. At the air quality site Fallmerayerstreet, the annual mean value (JMW. german for “Jahresmittelwert”) has been above the limit of 40µg/m³ since 2004 (Fig. 1.1).

![Figure 1.2](image_url)

**Figure 1.2:** The red shaded area represents the “non-attainment” zone where NO₂ levels exceed the regulative air quality limits. Especially the urban area of Innsbruck and Hall as well as the motorway are affected (taken from Land Tirol - TIRIS 2017. adopted by the author)  

Improved technology and better performance of vehicles does not seem to have changed this trend significantly (Moosmann et al. 2008, Beevers et al. 2012 and Carslaw et al. 2011). On the basis of NO₂ observations and emission models (e.g. Network Emission model. NEMO or Passenger car and Heavy duty Emission Model. PHEM. (Eichlseder and Rexeis 2005)) the Tyrolian government declared certain areas as non-attainment areas with special regulations. In Fig. 1.2 the map of Innsbruck and its surrounding areas are plotted. The red shaded patch is declared as a non-attainment area for NO₂. In Innsbruck and Hall, as well as along the A12/A13 motorway, the atmosphere is highly polluted due to excess levels of NO₂. While traffic is the dominant NO₂ source along motorways, additional NOₓ sources have to be considered in cities, for example, residential and commercial energy production and industrial sources. Annual concentration levels also vary from year to year because meteorological effects and conditions influence mixing and consequently the dilution of NOₓ (Weber et al. 2016).
In addition, Alpine valleys exhibit a smaller air volume and, especially, during winter strong inversions near the ground can lead to excess accumulation of pollution (Harnisch et al. 2008). Thus, these facts need to be considered for the interpretation of concentration trends. Innsbruck is influenced by a dominant valley wind system, which has been characterized by Vergreiner and Dreiseitl (1987). They also show that the valley circulation in combination with a limited air volume leads to a topographic amplification factor of nearly 3 (Vergreiner and Dreiseitl 1987).

NO$_2$ is a precursor substance of ozone and an effective way to improve air quality is to limit its concentration (Han et al. 2011). In the last decades, a range of models were developed which integrate our physical and chemical knowledge of the atmospheric evolution of pollutant gases. In combination with air quality observation networks we have the opportunity to investigate pollution trends and evaluate regulatory air quality strategies. Unfortunately, emissions are often poorly constraint and subject to large uncertainties’ (Colette et al. 2011). One problem is that traffic emission models are based on data which are mostly gathered under laboratory conditions, but real world emissions are often depending on the driving behaviour of drivers, driving speed, transport load, car type and other parameters. Therefore, a discrepancy between the measurements and calculated emissions is often observed (Beever et al. 2012). Ekström et al. (2004) evaluated the “COmputer Program to calculate Emissions from Road Transport (COPERT III)” model and found that emissions decrease slower in the real world than predicted by the model. Continuous observations and measurements of pollutants is therefore regarded as an important research priority in order to improve various emission models and inventories.

### 1.2 State of Research

In the last decades’ emission models have been extensively used to calculate and quantify levels of pollution. Especially traffic related pollutant emissions have received a lot of attention. Emission models are not only useful for scientific research but also play a pivotal role for national legislators, because these models serve as a basis for air quality legislation of pollutants (Smit et al. 2008). Smit et al. (2010) investigated over 50 studies of different emission models based on various concepts and concluded that
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we currently (2010) have a limited understanding of the uncertainties inherent to emission models. It was also pointed out that the mean prediction errors are strongly depending on the related gas. While carbon dioxide (CO₂) had a mean prediction error of 1.3, the factor was 2 for Hydrocarbon (HC) and NOₓ and up to 3 for carbon monoxide (CO) and Particulate Matter (PM). One problem for the evaluation of emission models in the past was the limited amount of measurement data (Smit et al. 2010). Although emission models use different upscaling methods to calculate emissions for inventories, the basis of all models is the same and relies on accurate knowledge of emission and activity factors. For mobile emission sources emission factors exhibit a characteristic range for each vehicle class, and regulatory limits are in place, which, in Europe are defined by the Euro Classes as seen in Fig. 1.3 (AQEG 2004).

Figure 1.3: Emissions for different vehicle types and euro classifications show a wide range. Fuel types play a significant role (taken from AQEG 2004)

The United States environmental protection agency’s (US EPA) notice of violation of the Clean Air Act to a German automaker regarding Diesel engines has sparked a number of new real world driving (RDE) emission tests across Europe, which show significant manufacturer and vehicle specific variability (Franco et al. 2014). Because nearly 60% (Statistik Austria 2017) of the car fleet in Austria is operated by Diesel engines the impact of uncertain knowledge of NOₓ emission factors may have a significant consequence for NOₓ immission levels.
1.3 Theoretical background

The theoretical background focuses on the theory of turbulence in the planetary boundary layer (PBL) and the chemical processes. The formation of NOx in the lower atmosphere and in combustion engines is briefly outlined at the end of this chapter.

1.3.1 The planetary boundary layer

The PBL (see Fig. 1.4) is the layer of the atmosphere which is “influenced by the surface of the earth directly and responds to changes of the surface with timescales of an hour or less” (Stull 1988). One characteristic of the PBL is that its expansion is variable in time and space and is influenced by fractional drag, evaporation, transpiration, heat transfer and flow modifications. The PBL can reach heights of some hundreds of meters up to a few kilometres (Stull 1988).

![Figure 1.4: Schematic illustration of the diurnal development of the PBL. During night a stable boundary layer (SBL) develops leaving a residual layer (RL) above. During day the SBL and RL are mixed forming the mixed layer. A capping inversion at to “top” represents the edge between PBL and free atmosphere (taken from Stull (1988), redesigned and adapted by the author).](image)

The PBL as well as all sublayers are characterized by strong vertical gradients of meteorological parameters which appear especially near the surface and at the top of the PBL (Arya 2001). With sunrise, the surface is heated and drives mixing of the air
above by the sensible heat flux. While the surface layer is mainly forced by superadiabatic conditions which induce turbulence and vertical mixing, quantities within the mixed layer tend to be constant over height following

\[
\frac{\partial q}{\partial z} = 0 \tag{1.1}
\]

where \( q \) is the individual variable (like water vapor, wind speed, ...), \( z \) the height above ground and \( \frac{\partial}{\partial} \) the partial derivation. The mixed layer (also called convective boundary layer) is the result of a growing entrainment zone between the surface layer and the residual layer of the previous night. With sunset, the sensible heat flux decreases and the surface cools down with an increase in stability near the ground which results in a stable nocturnal layer called stable boundary layer (Markowski et al. 2010).

### 1.3.2 The urban boundary layer

While rural areas are often influenced by vegetation or orography, the dominant character in urban areas are buildings. Therefore, the structure of the planetary boundary layer in these areas is different compared to that of rural areas. As it can be seen

![Figure 1.5: A schematic of the UBL at different scales. a) within urban zones the PBL consists of the UBL which is the sum of the surface layer and the mixing layer. b+c) on the local and microscale it can be seen that the schematic of the UBL is more complex especially near the ground. The surface layer is divided in the urban canopy layer (from ground up to the highest buildings) as part of the roughness sub layer and the inertial sublayer (taken from Shepherd (2005))](image-url)
in Fig. 1.5 the urban boundary layer (UBL) is growing downwind from the upwind edge of the city. While the UBL has its own flow characteristic, the area above the UBL is dominated by the upwind “rural” surface. From ground up to the rooftops the urban canopy layer (UCL) is dominated by buildings and street canyons with some vegetation. Within the UCL the air flow is very chaotic on the one hand but also structured due to ducting on the other hand. The layer above the UCL is the turbulent wake layer where wakes are affected by single buildings, multiple buildings and plumes transporting heat, humidity or pollutants (also called roughness sub layer in rural areas (Raupach 1979)). Within this layer relationships between flux profiles and Monin-Obukhov similarity theory are mostly invalid. It was shown by Roth (2000) that this layer can extend up to 2.5 to 3 times of the UCL. Subsequently to the turbulent wake layer is the urban surface layer or inertial sublayer (sometimes also called constant flux layer). The urban surface is characterized by constant turbulent fluxes. Individual wakes are subordinated while averaged effects of momentum und heat of the urban area have a great influence. Finally, the urban mixing layer represents the rest and extends up to the upper edge of the PBL. The urban mixing layer is more dominated by the heterogeneity of the urban surface than local scales. The diurnal fluctuation of the vertical extension of the UBL is similar to those of the rural boundary layer and mainly driven by radiation. Urban areas mostly have a heterogeneous surface caused by different land use which affects chemical processes significantly what is discussed later (Collier 2006).

1.3.3 Turbulence

“Air flow, better known as wind, can be divided into three broad categories: mean wind, turbulence and waves. Each can exist separately or in the presence of any of the others. Each can exist in the PBL where transport of quantities such as moisture, heat, momentum and pollutants is dominated in the horizontal by the mean wind and in the vertical by turbulence” (Stull 1988). Turbulence itself can be described as the superimposed gustiness part on the mean wind. It can be visualized by eddies with different sizes. The sum of magnitudes (= turbulent kinetic energy) of all different eddies gives us the turbulence spectrum plotted in Fig. 1.6. The spectrum can be divided into three parts: (1) the synoptic scale with its first peak (on the left side) which describes Rossby waves with an existence of some days, (2) a second smaller peak describing the diurnal cycles (day and night periods) and (3) the energy gap with a relatively low spectral
intensity. The right peak shows that especially the large scaled turbulent eddies are the most intense and with its motion they can generate smaller scaled eddies with a net turbulence energy transfer to the smaller ones. This process is better known as energy cascade. Finally, the energy dissipates into heat by molecular viscosity. A significantly small turbulent contribution in the spectrum is at about one hour. It is better known as spectral gap and separates the large scale, mostly driven by the mean horizontal wind, and the turbulent scale constituted by turbulence (Stull 1988). “The existence of the spectral gap allows us to partition the flow field in this manner” (Stull 1988).

Figure 1.6: the two main energy transport scales are shown. While the left peak is driven by global or mesoscale weather processes like large pressure systems, the second main energy transport peak is found in the turbulent scale and caused due to turbulent processes. In between there is an energy gap which is used to separate the synoptically and the turbulent scale per definition (taken from Stull (1988); modified version by the author)

1.3.4 NOx cycle within urban areas

Chemical processes are strongly influenced by emissions of the subjacent and surrounding surface. Chemical processes within and above urban areas differ from rural areas due to a dominant contribution from anthropogenic activities. Anthropogenic emissions are responsible for higher concentrations of many trace gases. Especially in
inner city areas where industry often plays a minor role the transport sector and domestic energy use are the main sources of \( \text{NO}_x \). The diurnal cycle caused by meteorology is also superimposed by human activities.

\( \text{NO}_x \) components emitted by cars are divided into primary \( \text{NO} \) (f-NO) and \( \text{NO}_2 \) (f-\( \text{NO}_2 \)). Apart from direct emissions from diesel driven cars the main portion of \( \text{NO}_2 \) in the atmosphere is formed by the oxidation of NO reacting with ozone

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2.
\]  

The conversion process depends on the amount of available NO and \( \text{O}_3 \) (AQEG 2004). In summer the speed of this reaction can take just 10 – 80s with typical ozone concentrations of 50 – 80ppb (Amt Kärntner Lreg. 2009). Because \( \text{NO}_2 \) is photochemically reactive, the oxidation reaction in eq. (1.2) leads to a built up during nighttime. When sunlight hits the \( \text{NO}_2 \) molecules one oxygen atom is split off and combines with molecular oxygen to form ozone. This so-called ozone regeneration can take place in presence of a third body (M), for example, with atmospheric nitrogen (\( \text{N}_2 \))

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}
\]  

\[
\text{O} + \text{O}_2(+\text{M}) \rightarrow \text{O}_3(+\text{M})
\]

(AQEG 2004). Eq. (1.2) – (1.4) define a photo stationary state where the formation of \( \text{NO}_2 \) is depending on the concentrations of NO and \( \text{O}_3 \) and the photolysis rate \( j_{\text{NO}_2} \)

where \( k \) is the reaction constant of eq. (1.2)

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

During daytime reactions of NO with free radicals such as hydroperoxy radicals (\( \text{HO}_2 \)) and organic peroxy radicals (\( \text{RO}_2 \)) formed from photochemical reactions of carbon monoxide and non-methane volatile organic compounds (NMVOC) regenerate \( \text{NO}_2 \) according to

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2
\]

\[
\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2.
\]

Eq. (1.6) and (1.7) counteract ozone depletion by eq. (1.2) resulting in an increase of net ozone production. Overall this will lead to higher ozone concentrations in air in the presence of \( \text{NO}_x \) and NMVOC (Amt Kärntner Lreg. 2009).
**Figure 1.7:** NO$_x$ cycle in urban areas where NO$_x$ is mainly emitted by traffic. Ozone is oxidized by NO during nighttime to form NO$_2$. Additional, NO$_2$ is formed by the free radicals HO$_2$ and RO$_2$ so that more ozone is produced than locally depleted (taken from AQEG (2004); modified version by the author).

### 1.3.5 NO$_x$ formation in combustion engines

**Formation of primary NO**

Nitric Oxide is the major proportion of NO$_x$ emissions caused by traffic (Amt Kärntner Lreg. 2009). A study from the Netherlands showed that the averaged primary emission of NO varies from 69-96% of total NO$_x$ emissions depending on roadside conditions. Cars driven with diesel, however, can reach NO$_2$/NO$_x$ ratios up to 70% (Keuken et al. 2012). Primary NO is produced by fuel combustion based on different chemical reactions. The thermal fixation of atmospheric Nitrogen (N) happens at high temperatures where oxygen (O, O$_2$) or hydroxyl radicals (OH) react with atomic or molecular nitrogen as

\[
N_2 + O_2 \rightleftharpoons 2NO \tag{1.8}
\]

\[
N_2 + O \rightleftharpoons NO + N \tag{1.9}
\]

\[
N + O_2 \rightleftharpoons NO + O \tag{1.10}
\]

\[
N + OH \rightleftharpoons NO + H \tag{1.11}
\]

Reaction (1.8) proceeds very slow, so it plays a minor role. The reactions given in eq. (1.9) and (1.10) are called Zeldovich Mechanism and are relevant in fuel lean combustions where O$_2$ concentration are large enough. One of the most important processes
is given in eq. (1.11) and probably predominant for NO formation based on thermal reactions (Flagan and Seinfeld 1988).

An alternative NO formation process is called “prompt NO” and was first described by Fenimore (1971). This process happens at lower temperatures and fuel rich conditions with short residence times. It is based on hydrocarbon radicals (CH) which react with atmospheric N to hydrogen cyanid (HCN) which forms cyanate (NCO) and oxygen and then NO

\[
\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N} \quad (1.12)
\]

\[
\text{HCN} + \text{O} \rightarrow \text{NCO} + \text{H} \quad (1.13)
\]

\[
\text{NCO} + \text{O} \rightarrow \text{NO} + \text{CO} \quad (1.14)
\]

(Flagan and Seinfeld 1988). It is noted that reactions can take place in both directions and therefore the complete formation process is more complex than described here.

**Formation of primary NO₂**

Miller and Bowman (1989) describe the primary NO₂ formation by HO₂ which react with NO to NO₂. Thereby the HO₂ is formed at lower temperatures diffusing to the region with higher temperatures where NO is formed.

\[
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \quad (1.15)
\]

A much slower reaction takes place when O₂ is oxidized by NO and therefore plays a less important role

\[
\text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O} \quad (1.16)
\]

(Kolar 1990). Beevers et al. (2012) showed that direct NO₂ emissions become more important because of the increased use of diesel driven cars. It has also been observed that the NO₂/NOₓ ratio has been continuously increasing for the past decade.
1.4 Goal and outline

As stated in the introduction, air quality management is one of the most important components of environmental regulation. Emission models are used to assess the environmental impact of pollutants and their output often influences political decisions on air quality regulatory actions. Especially in an urban area it is often difficult to quantify sources of pollutants because of uncertain knowledge of their emission strengths. Different approaches like the determination of emission ratios are usually used to validate bottom-up emission models but these are often only applicable to single emission sources. In this thesis, an extended approach to investigate Enhancement Ratios (EnR) for nitrogen oxides in an urban area (Innsbruck) is evaluated and compared to eddy covariance measurements. Additionally, the weekday and weekend effects are analysed and compared with traffic data as the transport sector is the dominant factor within the expected footprint. A profound analysis of the EnR for different intervals (here: monthly) should enhance the understanding of EnRs in an alpine city and investigate seasonal effects. Finally, a simple model is applied to the EnRs based on a traffic volume and domestic fuel weighting ratio.

Summary of the goals defined for this master thesis

(1) Characterization of the NO/NO\textsubscript{x} analyser Ecophysics CLD899Y
(2) Evaluation of the EnR approach by the flux ratio approach
(3) Analysing the weekday/weekend effect in conjunction with traffic volume
(4) Analysing the monthly development of the EnRs
(5) Comparison of the EnRs for two campaigns in 2015 and 2016
(6) Modelling EnRs based on a chemical mass balance approach
Chapter 2

2 Methodology

This chapter is divided into five sections. The first chapter deals with the characterization of the NO\textsubscript{x} instrument and is of technical nature while the second chapter describes the campaign data including related measurements. The third chapter handles post processing procedures of the recorded data and the fourth chapter describes the enhancement ratio approach by Yokelson et al. (2013), extending it to Turbulent Enhancement Ratios (TER). In the last section a simple emission ratio model, that is used later on, is introduced briefly.

2.1 NO\textsubscript{x} Instrumentation

The chemical luminescence detector (CLD899Y) was introduced by Eco Physics AG in 2011. The company is based in Switzerland and describes itself as a distributor of “innovative analytical solutions for measurement tasks in the fields of environment, health and process control” (EcoPhysics 2017a). The CLD899Y is part of the “CLD Supreme Line” and used for environmental applications, especially for tropospheric research, such as background ambient monitoring or investigating long range transport (EcoPhysics 2017b). The measured gases, NO and NO\textsubscript{x}, are detected by the chemiluminescence (CL) technique at 5Hz temporal resolution. NO\textsubscript{2} is calculated by subtracting NO from NO\textsubscript{x}. In the following sections the most important components of the instrument are described in more detail.


2.1.1 Measurement Principle

Chemiluminescence is the result of a chemical reaction of an exciting gas where light is produced by electrons falling back to their initial energy state. In general, only exothermic reactions are suitable for CL because of their sufficient energy generation (Baeyens et al. 1998). “As a principle in CL reactions, at least two reagents, A and B react to form a product C, some fraction of which is present in an electronically excited state, C*, which may subsequently relax to the ground state emitting a photon: (Baeyens et al. 1998)”

\[ A + B \rightarrow C' \rightarrow C + \text{hv} \]  

(2.1)

In general, most CL detectors are based on the homogenous gas-phase CL where the gas of interest [X] is mixed with a second reactant species [R] in the reaction chamber. The concentration I is given by

\[ I = k [R][X] \]  

(2.2)

where k is a factor proportional to the concentration I. If the second gas is added in sufficient excess its concentration can be considered constant and eq. (2.2) is reduced to

\[ I = k'[X] \]  

(2.3)

where k’ is the new proportionality factor and the concentration becomes directly proportional to the gas of interest (Cormier et al. 1973).

The CLD899Y operates at a wavelength bandwidth between 600 and 3000nm and a maximum intensity at about 1200nm (WM 2015). The reactant gas used is ozone (O₃) and the concentration I is proportional to the NO concentration.

**NO measurement**

In order to obtain NO concentrations, NO has to be converted to NO₂ according to the following reaction scheme

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  

(2.4)

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2^* + \text{O}_2 \]  

(2.5)
Thereby NO₂ appears in a ground and an excited state. While the ground state molecule is irrelevant for the CL measurement the NO₂* emits radiation while returning to the ground state

\[ \text{NO}_2^* \rightarrow \text{NO}_2 + h\nu \] (2.6)

Unfortunately, the largest amount of NO₂* is thermally quenched to the ground state by collisions with other molecules M

\[ \text{NO}_2^* + M \rightarrow \text{NO}_2 + M \] (2.7)

This so-called quenching process is an unwanted phenomenon of the CL technique (WM 2015). The efficiency of quenching “depends on the character of the colliding molecule M. For instance, water (H₂O) and carbon dioxide quench NO more effectively than nitrogen (N₂) and oxygen (O₂)” (WM 2015). To reduce quenching effects the pressure within the reaction chamber is reduced by a vacuum pump (i.e. a pressure of about 20mbar) to minimize the number of molecules (WM 2015).

**NO₂ measurement**

The NO₂ concentration is measured indirectly by measuring the NOₓ concentration and subtracting the NO concentration. To get the NOₓ concentration the amount of NO₂ in the sample gas has to be converted to NO first. This is achieved by a reducing agent which is described in more detail in section 2.1.2. The combined NO concentration (sum of true and converted NO) then flows to the reaction chamber where the same reaction takes place as described in the NO measurement section (WM 2015).

**2.1.2 Instrument Setup**

**Detector Unit**

The Detector Unit (DU) is the key component of the CLD899Y where the measurements of the gases are performed. The DU itself consists of the Photo Multiplier Tube (PMT) and the Main Reaction Chamber (MRC). For each channel the PMT is used to increase the weak signal of the MRC so it can be electrically detected. The PMT itself consists of a photocathode at the entry were a photon hitting the cathode emits an electron in the tube. This electron is multiplied by in series arranged dynodes which
are operating as electrodes. At the “end” of the tube the electrons hit the anode and flow towards ground through a resistor where the enhanced signal can be measured (Hamamatsu et al. 2007). One problem of PMTs is that electrons can spontaneously dissolve from the photocathode depending on the temperature of the PMT which is called dark current. To minimize that effect the PMT of the CLD899Y is cooled down to a temperature of -10°C (WM 2015).

**NO\textsubscript{2}/NO converter**

According to WM (2015) the CLD899Y NO\textsubscript{2}/NO converter is a thermally insulated steel block heated up to 375°C and containing the converter cartridge. To maximize the converter efficiency, the cartridge consists of a catalyst with a large surface (WM 2015). According to EcoPhysics (personal communication with Werner Moser) the CLD899Y used in this work consists of a molybdenum material for reduction of NO\textsubscript{2} in the presence of oxygen

\[
2\text{NO}_2 + 3\text{Mo} + \text{O}_2 \rightarrow 2\text{NO} + 3\text{MoO}_2 \tag{2.8}
\]

\[
\text{NO}_2 + \text{Mo} + \text{O}_2 \rightarrow \text{NO} + \text{MoO}_3 \tag{2.9}
\]

**Ozone Generator**

In order to fulfil the conditions required for the linearity of the concentration (see section 2.1.1) the CLD899Y has a built-in ozone generator (OG) to “produce” enough O\textsubscript{3} for the reactions in the main reaction chamber. The principle of the OG is based on the “silent electrical discharge method (SEDM)” as shown in Fig. 2.1 (WM 2015).

To generate O\textsubscript{3}, dry (to prevent reactions between water vapour and oxygen) gaseous oxygen molecules (O\textsubscript{2}) are decomposed and subsequent recomposed (Castle 1999). “However, it is well known that the energetics of the reaction show that it cannot be formed by a thermal activation process” (Castle 1999). Eg. (2.10) shows the formation and decomposition of oxygen and ozone (Castle 1999)

\[
3\text{O}_2 \rightleftharpoons 2\text{O}_3 \tag{2.10}
\]

The oxygen flows into the gap of the OG with a high voltage alternating electrical field. Due to free energetic electrons some of the molecules are split into their atomic form according to the following reaction (Sahoo et al. 2012)
\[
e^{-} + O_2 \rightarrow 2O + e^{-} \\
(\text{Castle 1999})
\]

Some of these single oxygen atoms combine with \(O_2\) to \(O_3\) in the presence of a catalyst \(M\) the reaction is

\[
O + O_2 + M \rightarrow O_3 \Delta H_{298}^{0} + M = +142\text{kJ/mol}
\]

(2.12)

Due to the fact that ozone formation is an endothermic reaction the SEDM is used to minimize the generated heat in order to avoid the decomposition of ozone (Sahoo et al. 2012). Additional free electrons also decompose ozone; this is why it is important to limit discharge activity. Reactions between oxygen and ozone as well as thermal losses of ozone lead to a maximal reachable ozone concentration of about 6% by weight according to Castle (1999). With the ozone produced in the OG the CLD899Y can assure a measurement linearity over six concentration decades for NO and NO\(_x\) (WM 2015).

**Ozone Scrubber**

Although \(O_3\) is a thermal unstable molecule and most of it decomposes while it is within the instrument it is necessary to ensure that \(O_3\) is completely removed from exhaust air. Therefore, the CLD899Y has an integrated Ozone Scrubber which works at a temperature of \(650^\circ\text{C} \pm 30^\circ\text{C}\) where the rest of \(O_3\) either becomes unstable and decomposes into molecular oxygen and atomic oxygen or reacts with other compounds in ambient air (WM 2015).
Pre-Chamber

The pre-chambers shown in section 2.1.3 are directly installed in front of each MRC. Via the application software (command: p_frequency) the solenoid valves can be switched so the flow of the sample gas is redirected to the pre-chamber. \( \text{O}_3 \) flows to the pre-chamber and reacts with the sample gas. According to the settings (p_frequency) the gas stays within the pre-chamber for a fixed amount of time before the valves are opened and flow is directed into the main reaction chamber. The pre-chamber reduces zero-drifts as well as minimizes cross sensitivity by other gases (WM 2015).

2.1.3 Gas Flow Schematic

The CLD899Y gas flow schematic shows the conceptual layout of the device as it was used during the operational phase (see Fig. 2.2). The instrument has two channels with two separate reaction chambers. According to experimental needs the pre-chamber can be switched off or on. Depending on this setting the sample gas flows directly to the DU or is first mixed with \( \text{O}_3 \) in the pre-chamber. The \( \text{NO}_x \) channel has a converter installed upstream to convert \( \text{NO}_2 \) to NO for further measurements. \( \text{O}_3 \) is generated within the instrument by the ozone generator and then transported to the pre-chamber and the reaction chamber. To prevent condensation, the PMT housing is continuously flushed by dry air. Due to the fact that \( \text{O}_3 \) is a toxic gas the ozone scrubber is used to destroy ozone before it is exhausted. The flow through the system and the necessary vacuum are sustained by an integrated vacuum pump at the end of the pipe assembly (WM 2015). Different flow restrictors and solenoid valves enable different operating modes such as calibration or measurements.
Figure 2.2: The gas flow schematic of the CLD899Y shows the most important parts of the instrument during “operation mode” (taken from WM (2015); modified version by the author)

2.1.4 Device Characterization

For further analysis of the data measured by the CLD899Y it is necessary to understand its behaviour under different conditions such as flow changes or different modes. The results of this device characterization are summarized below. Some limitations had to be considered though:

1) most laboratory tests were conducted only once which reduces the validity of the statistical analysis
2) calibrations are performed with Zero Air because the span calibration gas was missing and therefore replaced by a constant value for correction

Pressure Dependency

In the MRC the chemical reactions take place. One side effect of CL is quenching which is described in detail in section 2.1.1. To reduce this unwanted phenomenon a
vacuum of about 20mbar is generated in the MRC. As quenching can also influence the number of exciting molecules this can affect the concentration calculated from eq. (2.2). To investigate the vacuum in the MRC the default measurement setup of the campaign was changed according to Fig. 2.3.

Figure 2.3: The setup was especially designed for the MRC pressure test. A flow restrictor controlled the volume flow rate while the pressure of the sample-in pipe was measured by a flow meter (FM) and the pressure of the MRC was measured by the software of the CLD899Y. Each data was manually transferred to an Excel sheet and plotted (created by the author)

To “manipulate” the pressure within the manifold a flow restrictor was used to control the flow rate and thereby the pressure value. A flow meter was used to record the pressure within the manifold.

A pressure range between 450 and 950mbar within the manifold was chosen to investigate the MRC pressure dependence. 24 nearly equidistant pressure intervals were used to assure a good resolution of the pressure changes. To reduce statistical outliers four measurements for each manifold pressure were made. The result is shown in Fig. 2.4. The manifold pressure is labelled on the x-axis and the MRC pressure on the y-axis. The circles are the measurements and the solid line is the regression line (see section 2.4.1) of the scatter plot. A pressure dependency (concurrent with an altitude dependency) of the MRC is given in accordance to the manifold pressure. The pattern of the scatter plot implies a step function of the change of the MRC pressure. This is primarily caused due to the resolution of the built-in pressure sensor of the instrument. Lower manifold pressure led to a lower MRC pressure, where the MRC pressure change was 0.9mbar per 100mbar inlet pressure change (calculated from a linear fit). A number of studies (Tomita (2001) and Taupin et al. (2006)) showed that the rate of CL depends
on the pressure for different reactants. Because we used a critical orifice in the operational mode setting, the pressure variations within the manifold were reduced significantly and quenching effects due to pressure variations were negligible.

**Figure 2.4:** The scatter plot shows the result of the laboratory pressure test. It can be seen that within the laboratory pressure range an altitude dependency function exists in form of a step function. This occurs due to the resolution of the pressure sensor of the instrument.

**NOx Channel Correction**

The CLD899Y is a two-channel analyser where NO and NOx are measured simultaneously. After analysing the lag times between NO/CO2 and NOx/CO2 (see Fig. 2.5) by using the cross covariance between the gases it can be shown that there is a time difference of 0.8s between channel 1 (NO) and 2 (NOx) (see Fig. 2.6). As Fig. 2.2 shows, the only technical difference between the channels is the integrated NO2/NO converter of the NOx channel. While the classical measurement of the CLD899Y is

\[ \text{NO}_2(t) = \text{NO}_x(t) - \text{NO}(t) \]  

this has to be changed to

\[ \text{NO}_2(t_i) = \text{NO}_x(t_i + \Delta t) - \text{NO}(t_i) \]

where NO(t_i) is the true measurement for timestamp t_i, NOx(t_i+\Delta t) the true measurement for a timestamp which is delayed by the lag time \( \Delta t \) defined as
\[ \Delta t = \text{xcov}(\text{NO}_x, \text{NO})|_{t_{\text{min}}}^{t_{\text{max}}} = \langle \text{NO}_x, \text{NO} \rangle|_{t_{\text{min}}}^{t_{\text{max}}} \rightarrow \text{max}. \] 

(2.15)

t_{\text{min}} \text{ and } t_{\text{max}} \text{ define the bounds where the cross-covariance exhibits a local maximum.}

Fig. 2.5: The lag times between NO and CO\textsubscript{2}. (A), NO\textsubscript{x} and CO\textsubscript{2} (C) and NO\textsubscript{2} and CO\textsubscript{2} (E) are plotted for the entire campaign. The right-side panels show the averaged lag time for each period. Between channel NO and NO\textsubscript{x} a time lag of about 0.8s can be seen due to the technical setup of the CLD899Y. The periods are the result of a change in the measurement setup what changed the volume flow.

Fig. 2.6 shows the results of the correction given by eq. (2.13) to (2.15). We find a nearly symmetrical distribution around -0.8s (e.g. subplot B). After applying the time drift correction routine (C) most of the values are shifted to 0s delay. A small part of the data is, however, shifted elsewhere. This happens because the correction routine is automated and can fail when the cross-covariance between NO and NO\textsubscript{x} is increasing towards the time limits.
**Methodology**

**Figure 2.6:** (A) The black circles depict the original time delays between the NO$_x$ and NO channels while the red circles show the corrected values. (B) As the frequency of the instrument is maximal 5Hz the time shift is given in 0.2s intervals. (C) After applying the corrections the shift is removed.

**Calibration Check Correction**

In general, the CLD899Y uses calibration routines integrated in the software package. Further corrections cannot be easily implemented in the instrument software and have to be applied during post processing. Different procedures can be selected to perform these checks but will not be discussed here in detail. The laboratory setup when the instrument was operating in the “calcheck” (internal name, standing for calibration check) mode is shown in Fig. 2.3. A complete calibration check contains two measurement phases interrupted by a flushing phase where the pipes of the instrument are “cleaned” from remaining gas samples. During each measurement phase a different calibration gas with known chemical composition was measured. Offset measurements are done by calibrating with Zero Air while measurement range corrections are done with the span calibration. While the intervals can be set manually the flushing task took 10s and the calibration task 20s respectively. An overall procedure was finished after 60s (WM 2015). The reference pressures in the manifold ranged between 450-
920mbar with five slightly varying intervals. The number of measurements were equal to those described under “Pressure Dependency” section. The function of the pre-chamber is described in section 2.1.2. The results are plotted in Fig. 2.7. The manifold pressure (x-axis) is plotted against the NO concentration (y-axis) without pre-chamber (A, C) and with activated pre-chamber (B, D). Zero air calibration values are plotted at the top (A, B) and span calibration values are given at the bottom (C, D). The blue values indicate the measurement points.

**Figure 2.7**: The NO concentration is measured for six different pressure levels in the manifold. The manifold pressure is plotted on the x-axis, the concentration for different calibration checks on the y-axis.

While the span check with the span gas (ref. 909ppb) has nearly a perfect linearity without any spread, the spread in the zero check with the zero gas (ref. 0ppb) is higher. Effects of the pre-chamber during span check is negligible while there is a big effect on zero check as the manufacturer stated. The pre-chamber indeed reduces the zero offset to 0.1ppb (regarding to the manifold pressure). A strong positive pressure dependency during span calibration (C, D) is observed regardless of the pre-chamber mode, with an R² of 99%. The NO concentration is changing about 60ppb per 100mbar pressure change. The reason for this pressure dependency as described in detail in “Pressure Dependency” in section 2.1.4.
As zero gas does not contain any nitric oxide the zero correction should show values near the zero point. Comparing Fig. 2.7, A and B suggests a different pressure dependency depending on the pre-chamber function. In general, the zero offset is about 3.28ppb (within the tested pressure range) without pre-chamber and 0.1ppb with activated pre-chamber. This improvement was expected as the pre-chamber improves the photon yield of the CL due to better mixed gas. While there is a slightly negative slope of 0.01ppb per 100mbar pressure change with deactivated pre-chamber a positive slope of 0.07ppb is observed with pre-chamber. Due to the relatively large scatter and the small number of data points the $R^2$ is just 9% for zero correction without pre-chamber and 35% with pre-chamber. All data used for further processing of this master thesis were corrected based on these findings.
2.1.5 Specifications

The specifications of the CLD899Y analyser, taken from the operator’s manual in Version 1.0 8th of January 2015 and are summarized as following.

**Table 2.1: Performance specifications of the CLD899Y**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value/Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement ranges selectable(^{1}) from</td>
<td>0.0-1ppb to 0-1000ppb</td>
</tr>
<tr>
<td>Detection limit (2σ)</td>
<td>0.05% of max range(^{2})</td>
</tr>
<tr>
<td>Signal noise</td>
<td>0.5% of measurement value(^{3})</td>
</tr>
<tr>
<td>Interferences</td>
<td></td>
</tr>
<tr>
<td>water vapour(^{3})</td>
<td>&lt;3% per Vol-% H(_2)O (dep. on type of analyser and options)</td>
</tr>
<tr>
<td>carbon dioxide(^{3})</td>
<td>&lt;1% per Vol-% CO(_2) (dep. on type of analyser and options)</td>
</tr>
<tr>
<td>Lag time</td>
<td>&lt;2s</td>
</tr>
<tr>
<td>Rise time (0-90%)</td>
<td>&lt;1s</td>
</tr>
<tr>
<td>Fall time (100-10%)</td>
<td>&lt;1s</td>
</tr>
<tr>
<td>Zero-point drift</td>
<td>&lt;0.1% of max. range/day</td>
</tr>
<tr>
<td>Sensitivity drift</td>
<td>&lt;1%/day</td>
</tr>
<tr>
<td>Response times(^{4})</td>
<td>&lt;1-3s dependent on type of analyser and options</td>
</tr>
<tr>
<td>Linearity within range</td>
<td>&lt;1% of point from 6% to 100% of range</td>
</tr>
</tbody>
</table>

\(^{1}\) each 2 different ranges can be chosen  
\(^{2}\) Filter setting “slow” (CLD899Y set to 30s). Specified value depending on filter setting.  
\(^{3}\) Data in % of measurement value  
\(^{4}\) Data in [s] for: lag time, rise time (0-90%) and fall time (0-90%)
Table 2.2: Operating specifications of the CLD899Y

<table>
<thead>
<tr>
<th>Description</th>
<th>Value/Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical data</td>
<td></td>
</tr>
<tr>
<td>Power uptake</td>
<td>400-600VA max.</td>
</tr>
<tr>
<td>Mains voltage</td>
<td>100-230V/50-60Hz</td>
</tr>
<tr>
<td>Installation/overvoltage category</td>
<td>II</td>
</tr>
<tr>
<td>Analog outputs</td>
<td></td>
</tr>
<tr>
<td>(available on external USB-Box)</td>
<td>0 to 10V (500kΩ min.)</td>
</tr>
<tr>
<td></td>
<td>0 to 20mA (500Ω max.)</td>
</tr>
<tr>
<td>Analog inputs and digital I/O</td>
<td>available on external USB-Box</td>
</tr>
<tr>
<td>Permitted ambient temperature</td>
<td>5 to 40°C</td>
</tr>
<tr>
<td>Permitted humidity range</td>
<td>5 to 95% RH (non condensing)</td>
</tr>
<tr>
<td>Operating altitude</td>
<td>up to 2000m above sea level</td>
</tr>
<tr>
<td>Pollution degree</td>
<td>2</td>
</tr>
<tr>
<td>Converter Type</td>
<td>Y</td>
</tr>
<tr>
<td>Converter temperature</td>
<td>377°C</td>
</tr>
<tr>
<td>NOx efficiency</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>at max. NOx</td>
<td>100ppb</td>
</tr>
<tr>
<td>Ammonia efficiency</td>
<td>&lt;4%</td>
</tr>
<tr>
<td>at max. Ammonia</td>
<td>0.1ppm&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Life expectancy of converter</td>
<td>10000h</td>
</tr>
<tr>
<td>Reaction chamber temperature</td>
<td>50°C, regulated</td>
</tr>
<tr>
<td>PMT temperature</td>
<td>-10°C, regulated</td>
</tr>
<tr>
<td>Reaction chamber pressure</td>
<td>20±5mbar abs.</td>
</tr>
<tr>
<td>Inlet pressure range&lt;sup&gt;2&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Sample gas</td>
<td>ambient pressure</td>
</tr>
<tr>
<td>Calibration gas with option v2/v8</td>
<td>2-3bar abs.</td>
</tr>
<tr>
<td>Sample flow (total&lt;sup&gt;3&lt;/sup&gt;, without pressure regulation)</td>
<td>700ml/min</td>
</tr>
<tr>
<td>Humidity range of sample gas</td>
<td></td>
</tr>
<tr>
<td>without option h</td>
<td>&lt;95% RH of ambient temperature</td>
</tr>
<tr>
<td>with option h</td>
<td>&lt;30 Vol-% H2O</td>
</tr>
</tbody>
</table>

<sup>1</sup> or 10% of range
<sup>2</sup> calibration gas pressure and sample gas pressure without internal pressure regulation must not deviate by more than 1mbar in order to fulfill the specifications
<sup>3</sup> depending on model & version
2.2 Field Campaign

The field campaign iNNAQS, which stands for iNNsbruken Air Quality Study, was conducted (2015) with the “goal to quantify “reactive trace gases” (NMVOC, CO₂, CO, NO, NO₂) and aerosol number fluxes (total in size-resolved 6nm-10µm) at an urban location in downtown Innsbruck” (Karl et al. 2017). The study took place from July 10th to October 20th 2015.

2.2.1 Field Site

Field measurements were performed at the top of the Bruno-Sander house (11.385489°E, 47.264167°N, WGS84, 560m a.s.l.) at the University of Innsbruck. The area is characterized by urban structures such as buildings (up to 30m), roads and small patches of vegetation (mostly lawns, bushes and broadleaf trees along alleys). The site is generally quite suitable for micrometeorological studies, with the mean measurement height about twice the surrounding building heights. Only one University building in the west (at a distance of about 50m), one in the south (University clinic for plastic surgery, distance about 350m) and one in the southeast (University clinic for gynaecology, distance about 250m) are about the same height of the measurement tower and can influence the flow under certain circumstances. In the northwest of the building the Inn river is passing from southwest to northeast. One of the busiest crossroads of Innsbruck (Innrain-Anichstreet) intersects in the south sector.

2.2.2 Setup

Fig. 2.8 gives a schematic overview about the system setup used during the campaign.
**Methodology**

Figure 2.8: Schematic system setup during the iNNAQs campaign in July-September 2015 (created by the author, photo by M. Graus (2015))

**Manifold**

The inlet for the CLD899Y was positioned on top of the monitoring station at a tower, elevated approximately 48m above street level. The diameter of the manifold was 1/8” and consisted of a 10m long Perfluoralkoxy-Polymere Teflon tube (PFA) purged by a flow rate of 10l/m resulting in a pressure of 714mbar within the tube. To prevent water vapour formation and any excessive temperature fluctuation, the manifold was wrapped with an isolation material and constantly heated to about 40°C. To prevent contamination of the trace gas measurement manifold the aspirated sample air was filtered by a particulate filter.

**Route Section**

The route section represents a part of this setup that allows to connect a variety of measurement instruments to the manifold. It consists of T-pieces also made of PFA Teflon which are connected in series. To reduce pressure fluctuations in the manifold, caused by the pump, a critical orifice was placed in between the route section and the CLD899Y.

**Measurement Instrument**

The CLD899Y was connected to the end of the tube of the manifold. Additional O₂, NO and Zero Air gases were connected directly to the instrument allowing the generation of ozone and calibration checks.
Beginning in July 2015, highly time resolved measurements of NO\textsubscript{X} concentrations were recorded continuously by the CLD899Y. In addition, fast CO\textsubscript{2} measurements were conducted by the Campbell CPEC200 system, which also included a CSAT3 Sonic anemometer. All standard meteorological parameters were recorded by the ZAMG weather station situated at the top of a second tower. A complete overview of measurement systems relevant to this thesis is given in Table 2.3.

Table 2.3: List of all measured variables at the iNNAQS campaign

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Duration</th>
<th>Used instruments</th>
<th>temporal resolution</th>
<th>Measured gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>iNNAQS</td>
<td>July – October 2015</td>
<td>Eco Physics CLD899Y</td>
<td>5Hz</td>
<td>NO, NO\textsubscript{X}, NO\textsubscript{2} \textsuperscript{1)}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Campbell CSAT3 Sonic</td>
<td>10Hz</td>
<td>3D wind vector</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Campbell CPEC200</td>
<td>10Hz</td>
<td>CO\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Weather Station</td>
<td>1min\textsuperscript{2)}</td>
<td>standard meteorological parameters</td>
</tr>
</tbody>
</table>

\textsuperscript{1)} NO\textsubscript{2} is not measured but calculated by subtracting NO\textsubscript{X} - NO
\textsuperscript{2)} the accessible data are stored in 1min
2.3 Data processing

The calculation of the turbulent enhancement ratio was based on the eddy covariance method following Lee et al. (2005) with some adaptations for the iNNAQs campaign:

(1) *Data framework:* the whole dataset started on July 1st, 2015 00:00:00.000 and ended on October 20th, 2015 23:59:59:800. The averaging time of each interval was set to 30min with the timestamp at the beginning of the interval. A quality flag, described later in more detail, is used to meet the required conditions for turbulence and stationarity. A threshold to limit the number of missing values during each interval to a maximum of 10% (= 0.1) was also implemented as a quality exclusion flag.

(2) *Data preparation:* the raw data of the CLD899Y were corrected as described in more detail in section 2.1. Data of the Campbell CPEC200 system and meteorological data were used as they were uploaded to the internal iNNAQs data archive. Eddy covariance flux data were obtained from Marcus Striednig, University of Innsbruck.

(3) *Data assimilation:* NO, NO\(_x\), NO\(_2\) were resampled and interpolated to a predefined time stamp and time period as required. Data gaps were replaced by NaNs (Not a Number) so the missing values did not have an influence on subsequent calculations. Corrections were made on the basis of calibration checks performed every day at midnight. Span calibration was not available and therefore corrected afterwards according to findings given in section 2.1.4 (Calibration Check Corrections). A constant correction factor of 1.2402 for NO and 1.2020 for NO\(_x\) was adopted to account for the pressure corrected span calibration.

(4) *Averaging:* for Reynolds decomposition, the mean of each time interval of each trace gas is given as

\[
\bar{C} = \frac{1}{n} \sum_{i=1}^{n} C_i
\]  

(2.16)

where \(\bar{C}\) is the mean concentration over a 30min interval, and \(C_i\) represents individual measurements within the averaging interval. The number of samples was 9000 for a data acquisition frequency of 5Hz.

(5) *Separation/Reynolds decomposition:* in order to perform Reynolds decomposition the mean is subtracted from the actual value to get the fluctuating part
Methodology

\[ C(t)' = C(t) - \bar{C}(t_n) \]  \hspace{1cm} (2.17)

where \( C' \) is the fluctuating part, \( C \) the actual measurement, and \( \bar{C} \) the mean over the averaging period (see Fig. 2.10).

\[ Q_{AQC} \]: the quality flag for quality assurance and check (QAQC) is described in section 2.3.1.

(7) Calculations: calculation of the EnR approach is lined out in section 2.4.

2.3.1 Quality Assurance and Check

It is well established that the eddy-covariance method works best under turbulent conditions. One consequence is often, that fluxes are often underestimated during nights with low wind speeds and stable stratification (Papale et al. 2006). Before correlating and validating EnR with flux ratios (FR) it is therefore necessary to apply appropriate QAQC criteria. A quality flag is defined by a combination of different criteria, which should also fulfil the conditions for well-developed turbulence. In the following section these selection criteria are discussed in more detail.
**Steady State Criteria**

One problem when calculating fluxes can be due to non-stationary conditions. In these cases different conditions during the averaging interval lead to a violation of the basic assumption, that mean and turbulent parts can be separated clearly, which makes a physical interpretation more difficult. Large perturbations during an averaging interval are often indicative of nonstationary conditions. To assure steady state conditions, a test based on Gurjanov et al. (1984) and used by Foken and Wichura (1996) is implemented. Thereby the covariance between the averaging period and the averaged covariance of fractional intervals of the averaging time are compared (Lee et al. 2005). The interval $t_{\text{frac}}$ for a 30min averaging time $t_{\text{ges}}$ is chosen as 5min as described by Lee et al. (2005). The averaged covariance on the 30min interval is given as

$$w'X' = \frac{1}{M} \sum_i (w'X'_i)$$  \hspace{1cm} (2.18)

where $(w'X'_i)$ is equal to eq. (2.35) for $t_{\text{frac}}$ and $M$ is defined as

$$M = \frac{t_{\text{ges}}}{t_{\text{frac}}} \rightarrow \frac{30}{5} = 6.$$  \hspace{1cm} (2.19)

The reference covariance $(w'X)'_0$ is also given in eq. (2.35) with a different amount of measurement points based on $t_{\text{ges}}$ (9000points for 5Hz over 30min) (Lee et al. 2005). According to Lee et al. (2005) steady state conditions can be assumed when the difference between the averaged covariance and the reference covariance $RN_{\text{cov}}$ is smaller than 0.3. This threshold is based on empirical experience and was confirmed by other authors (Foken and Wichura 1996).

$$RN_{\text{cov}} = \left| \frac{w'X' - (w'X)'_0}{(w'X)'_0} \right| < 0.3|_{\text{steady state}}$$  \hspace{1cm} (2.20)

In Fig. 2.11 the amount of discarded values is plotted as a ratio for all 30min interval. A diurnal cycle with higher values during night and lower values during day is evident. The maximum is reached during the 23:30UTC interval with nearly 50% of all values being discarded. The minimum is 1% between 12UTC and 14:30UTC. Between 6:30UTC and 14:30UTC about 97% of the data are valid. Due to high atmospheric stability during the night, turbulent motions are suppressed which is a main reason for the larger fraction of rejected data. Between 15UTC and 6UTC 10% to 45% of the data are discarded by the stationarity criteria.
Signal to Noise Ratio

A challenge for measurement devices is the reliability of the result at low concentration levels where the limits of detection of the instruments are reached. It is the point where the measured concentration of a gas cannot be distinguished from the absence of the gas (often called blank value) (Shrivastava and Gupta 2011). The measured signal $S_t$ is the sum of the observed signal $S_x$ plus a background response $S_b$

$$S_t = S_x + 3S_b$$  \hfill (2.21)

$S_b$ can be estimated by making separate measurements with a calibration gas (Paccagnella and Murphy 1982). The limit of detection (or detection limit $L_D$, LOD) is illustrated quite well in Fig. 2.12. Each signal of the instrument of the blank and a sample gas is assumed to be normally distributed (Case et al. 2004). The mean represents the true value. If the LOD is defined based on the signal-to-noise ratio it is often defined as

$$LOD = \left| \frac{\bar{x}}{\sigma_{\text{noise}}} \right| < 3$$  \hfill (2.22)

where $\bar{x}$ the mean of the measured pollutant concentration and $\sigma_{\text{noise}}$ is the noise for the background (blank) measurement. In the literature, it is widely accepted to use an LOD smaller than $k=3$ as threshold. This means that in 99.7% of all cases a measured value is different from the blank value within the confidence interval [-k. k]. Or in other words the significance level is 0.3% (personal communication with M. Graus).
Figure 2.12: Illustration of the Limit Of Detection (LOD, \(L_D\)) and the blank value (mean=0). The decision whether a blank value is met or not is defined by the Critical Level (\(L_c\)) (taken from Currie (1984); modified by Case et al. (2004) and the author)

2.4 The Enhancement Ratio Approach

In general, pollutant plumes disperse due to dilution within the atmosphere caused by mixing with background air. Consequently, this fact leads to a strong temporal dependency of the concentrations which are measured by the instruments. Especially for analysing sources of certain tracers in the PBL this background information or dilution is dominated by meteorology (Yokelson et al. 2013). As an example, Fig. 2.13 depicts diurnally averaged concentrations of \(\text{NO}_x\) versus carbon dioxide. Under the assumption that \(\text{CO}_2\) and \(\text{NO}_x\) have the same dominant sources and sinks as well as identical atmospheric lifetimes (thus background levels), the correlation between the mean concentrations of these trace gases should be nearly constant. Panel B in Fig. 2.13 though shows that the correlation between measured \(\text{NO}_x\) and \(\text{CO}_2\) throughout a day is subject to significant variations. The reason for this can be found in pronounced differences of the evolution of their diurnal concentrations. For example, \(\text{NO}_x\) (Fig. 2.13, A) is strongly influenced by traffic and therefore varies with the daily traffic load within the footprint. \(\text{CO}_2\) (Fig. 2.13, C) has a well-known daily course with a maximum in the early morning hours and a minimum in the afternoon caused by vegetation and the evolution of the PBL.

For the purpose of characterization of \(\text{NO}_x\) sources within Innsbruck it is necessary to find an approach that excludes effects from local and mesoscale variability. A lot of
studies (e.g. Horst et al. (2004), Oncley et al. (2007), Foken et al. (2010), Patton et al. (2011)) have used the Eddy Covariance Method which is fairly well evaluated. Here we wanted to focus on a complementary approach based on the enhancement ratio approach which is often used for plume characterisation studies of single point sources.

**Figure 2.13:** (A) Diurnal NO$_x$ mixing ratio. The two local peaks in the morning and afternoon are corresponding with the local traffic and the rush-hours. (B) Scatter plot between the NO$_x$ and CO$_2$ mixing ratio. A hysteresis loop suggest that meteorological effects play a key role when analyzing trace gas sources within Innsbruck. (C) Diurnal CO$_2$ mixing ratio which is affected by the daily PBL extension and photosynthesis.

EnR (or $\Delta X$) are calculated by subtracting the background of the species of interest and calculating

$$\text{EnR}_X = \Delta X = X - X_{bg}$$  \hfill (2.23)

where $X$ is the true measurement and $X_{bg}$ the background mixing ratio (mol/mol). The normalized enhancement ratio is then calculated by dividing EnR$_X$ with a reference species $Y$ (given as $\Delta Y$). which is obtained the same way as for $\Delta X$.

$$\text{EnR}_{X/Y} = \frac{\Delta X}{\Delta Y} = \frac{X - X_{bg}}{Y - Y_{bg}}$$ \hfill (2.24)

Here we select a relatively stable “trace gas” such as CO$_2$ or CO as reference $Y$. One problem with eq. (2.24) is that it requires two measurements for each species. On
the one hand the measurement within the plume and on the other hand the measurement of background air. While the first one is generally easily obtained, the last one is often not available during campaigns. EnR$_{X/Y}$ has then to be obtained by a regression analysis of the time series of X and Y (Yokelson et al. 2013).

2.4.1 Principle of least squares

The following section is taken from Weatherburn (1968) and Fisher (1970) and modified by the author. The principle of least squares describes a fitting method where the linear regression line follows the relation (see Fig. 2.14)

\[ \Delta = \sum_{i=1}^{n} \Delta^2 = \sum_{i=1}^{n}[mx_i + b - y_i]^2 \equiv \min. \]  

(2.25)

where \( m \) is the regression slope, \( b \) the \( y \) intercept within the Cartesian plane and \( x_i \) and \( y_i \) are the experimentally determined pairs of values, \( \Delta \) represents the difference between the true measurement \( y_i \) and the regression and \( \Sigma \) is the summation operator.

According to eq. (2.25) the partial derivatives of the unknown coefficients \( m \) and \( b \) have to be zero. Applying

\[ \frac{\partial \Delta}{\partial m} \equiv 0 \]  

(2.26)

\[ \frac{\partial \Delta}{\partial b} \equiv 0 \]  

(2.27)

on eq. (2.25) results in

\[ 2 \sum_{i=0}^{n}[mx_i + b - y_i]x_i = 0 \]  

(2.28)

\[ 2 \sum_{i=0}^{n}[mx_i + b - y_i] = 0 \]  

(2.29)

what can be rewritten to

\[ m \sum_{i=1}^{n} x_i + b \sum_{i=1}^{n} x_i = \sum_{i=1}^{n} x_i y_i \]  

(2.30)

\[ m \sum_{i=1}^{n} x_i + nb = \sum_{i=1}^{n} x_i. \]  

(2.31)

The solution of the system of equations of (2.30) and (2.31) for the unknown coefficients \( m \) and \( b \) are

\[ m = \frac{\sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i - n \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{(\sum_{i=1}^{n} x_i)^2 - n \sum_{i=1}^{n} x_i^2} = \frac{\sum_{i=1}^{n} x_i y_i - \frac{1}{n} \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{\sum_{i=1}^{n} x_i^2 - \frac{1}{n} (\sum_{i=1}^{n} x_i)^2} \]  

(2.32) and

\[ b = \frac{1}{n} (\sum_{i=1}^{n} y_i - m \sum_{i=1}^{n} x_i). \]  

(2.33)
Defining the variance of species X as

\[ \text{VAR}(X) = \sum_{i=1}^{n} (x_i - \bar{x})^2 = \sum_{i=1}^{n} x_i^2 - \frac{1}{n} \left( \sum_{i=1}^{n} x_i \right)^2 \] \hspace{1cm} (2.34)

the covariance between species X and Y as

\[ \text{COV}(X, Y) = \sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) = \sum_{i=1}^{n} x_i y_i - \frac{1}{n} \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i \] \hspace{1cm} (2.35)

so, eq. (2.32) can be rewritten as

\[ m = \frac{\text{COV}(X, Y)}{\text{VAR}(X)} = \frac{\langle X, Y \rangle}{\langle X^2 \rangle}. \] \hspace{1cm} (2.36)

![Figure 2.14](image)

**Figure 2.14:** the principles of least squares minimizes the errors \( \Delta_i \) between the true measurement and the regression line

The regression slope \( m \) is obtained according to eq. (2.36), which is defined as the division of the covariance between \( X \) and \( Y \) by the variance of reference species \( Y \).

Central to this master thesis we define the EnR as a TER between \( \text{CO}_2 \) and \( \text{NO}_x \) according to

\[ \text{EnR} = \frac{\text{COV} \left( \frac{\text{CO}_2}{\text{NO}_x} \right)}{\text{VAR} \left( \frac{\text{CO}_2}{\text{NO}_x} \right)} = \frac{\langle \text{CO}_2 \text{NO}_x \rangle}{\langle \text{CO}_2^2 \rangle}; \] \hspace{1cm} (2.37)

### 2.5 Emission Ratio Model Setup

Experimentally obtained turbulent enhancement ratios can be used to test emission ratios inferred from bottom-up emission models. This thesis is using the approach by Karl et al. (2017). A nonlinear minimization routine unmixes two end-members under certain conditions (boundary conditions). As EnRs represent the ensemble mean of the
combination of different emission sources within the turbulent footprint, the two end-members can be calculated from a regression based on

\[ a_{x_1} r_1 + a_{x_2} r_2 = r_{mx} \]  

(2.38)

where \( a_{x_i} \) are the activity factors of each single end-member, \( r_i \) are the emission ratios and \( r_{mx} \) are the calculated EnR. Additionally, the constraint

\[ a_{x_1} + a_{x_2} = 1 \]  

(2.39)

must be fulfilled as just two members are accepted here (Karl et al. 2017). The routine is based on a Matlab nonlinear programming solver called “fmincon”. Details are described in Byrd et al. (2000). The routine finds a minimum of \( f(x) \) under following conditions

\[
\min_{x} f(x). \begin{cases} 
  c(x) \leq 0 \\
  A \cdot x \leq b \\
  lb \leq x \leq ub
\end{cases}
\]

(2.40)

where \( c(x) \) are nonlinear functions. “lb” and “ub” the lower and upper bounds and A and b the linear inequality constraints (MathWorks 2017).
Chapter 3

3 Results and Discussion

The following section discusses the campaign meteorology where most of the data were taken from ZAMG (2015), as well as an analysis of traffic patterns, relevant to the interpretation of NO$_x$ emission sources. The results of the daily concentrations of NO$_x$ and its compounds can be found in subsection three. Next the enhancement ratio approach is evaluated and the daily EnRs for the field site are being put into context of a simple model based on a nonlinear optimization approach. I will also present a comparison with a campaign conducted in 2016.

3.1 Campaign meteorology

The campaign covered the summer and autumn seasons from July to October. This period was characterized by multiple hot periods with temperature maxima beyond 30$^\circ$C. Just before the campaign start on July, 7$^{th}$, the absolute maximum temperature ever recorded in Innsbruck (since 1877) was 38.2$^\circ$C. The maximum temperature within the campaign period was 35.3$^\circ$C on July, 17$^{th}$. The absolute minimum temperature was 3.2$^\circ$C on October, 1$^{st}$. The average daily maximum (and minimum) temperature was 22.8$^\circ$C at 12:30UTC (and 13.4$^\circ$C at 4UTC). During the campaign the total precipitation at the University of Innsbruck was 391.6mm. This is close to the long-term average. Especially in the summer months thunderstorms caused most of the precipitation. The daily global radiation at the field site was 772Wm$^{-2}$ at 11UTC. The maximal measured value was 1293Wm$^{-2}$ on July 31$^{st}$. The daytime minimum (4-18UTC) was 45Wm$^{-2}$. Due to the fact that the campaign lasted nearly four months, the sunrise and
Results and Discussion

Sunset times changed from 3:30 to 4:45UTC for sunrise and from 17:45 - 19:15UTC for sunset. In the following the campaign months are described in more detail.

July 2015 was the hottest month since measurements began in Innsbruck in 1877. The month started with a hot period starting at the end of June lasting for eight days. It was the hottest week with daily averaged temperatures around 25°C. The second hot period occurred from July 11th to 24th. The end of July was cooler than the climatological average (1981-2010). In general, July was 3.5°C (Ø 18.3°C) warmer at University of Innsbruck than on average. Although the monthly precipitation was close to the average climatological trend, the period between July 9th and 21st was explicitly too dry. Precipitation at the field site was recorded on 18 days. Most of the rainfall was caused by thunderstorms. Precipitation with more than 10mmd⁻¹ happened on July 8th, 22nd and 25th. More than 30mmd⁻¹ fell on July 23rd. In general, thunderstorms were short in time and local so that they did not significantly affect the sunshine duration. According to ZAMG (2015) the sunshine duration in Tyrol was 22% above the long-term average. Using a Foehn classification by Plavcan et al. (2014) five Foehn events were identified in July.

August was characterized by two hot periods. The first one started on August 3rd and lasted until August 15th, while the second one occurred from August 27th well into September. The average daily temperature was 20.5°C in August. On 13 days precipitation was recorded with three days more than 10mmd⁻¹ and two days more than 20mmd⁻¹. The amount of precipitation was nearly equal to the climatological trend. Mostly thunderstorms were responsible for precipitation events in August. Especially rain events around August 14th were triggered by a front system with embedded thunderstorms. Sunshine duration in Tyrol during August was 12% higher than the climatological mean. On eight days Foehn events were recorded.

Temperatures during September were highly variable leading to climatological average conditions during this month. While the first three days in September still belonged to the heat period of August, the days up to the September 10th were below the climatological average. A period of eight days with warmer temperatures up to September 19th was followed by a cold period by the end of the month. This led to an average temperature of 13.7°C and therefore 0.6°C beneath the climatological mean. Eleven precipitation events were recorded where four events were with more than 10mmd⁻¹ and one with more than 20mmd⁻¹. The most amount of precipitation was
caused by frontal systems. This is also the reason why the sunshine duration was 12% lower than the average. On seven days of September Foehn events occurred.

October data are only available up to the 20th. The mean temperature of the month was 10.5°C. On eleven days precipitation was recorded but just one event with more than 10 mm d⁻¹ (14th). The monthly amount of rain was almost reached on the 20th. The sunshine duration was 10% below average values. Within the first twenty days, four Foehn events were classified at the beginning of the month (September 1st – 4th).

![Figure 3.1](image)

**Figure 3.1:** The meteorological parameters are recorded by the “TAWES” station of the ZAMG next to the tower on the top of the Bruno-Sander house. (A-B) are representing daily temperature values. (C) is 6h-global radiation and (D) the averaged daily global radiation. (E) shows the 6h-wind speed, and (F) the mean daily wind speed. (G) is the daily precipitation rate and (H) the cumulated rain amount.

In Innsbruck typical wind systems are affected by the surrounding topography. Predominant wind sectors are around 60° which corresponds to valley-up winds and 225° which is the wind direction for valley-down winds. As the wind is blowing from the Wipp valley from about 180° during Foehn events, this wind direction is the third dominant sector.

The results of the wind analysis are shown in Fig. 3.2 where the months of the campaign are separately plotted. On Fig 3.2, panel A1-4 the daily horizontal wind
speed (ff) is plotted and in panel B1-4 the diurnal wind direction (dd) is illustrated. The bottom graphs in Fig. 3.2 are the relative distribution of the wind sectors. The sectors themselves are divided into 20° intervals.

A daily course of the wind speed can be seen for all months where the minimum speed is during nighttime and the maximum during daytime. Nighttime wind speed is between 0.3 and 1.3 ms\(^{-1}\) with higher averaged wind speeds in September and October. The daily maximum speed is depending on the month and is 3.9 ms\(^{-1}\) in July and September. August has a maximum averaged wind speed of 3 ms\(^{-1}\) and the lowest value was observed in October with 2.6 ms\(^{-1}\). The increase of wind speed correlates with a change of wind direction between 9–11 UTC.

The wind direction as stated before is affected by the direction of the Inn valley. In July the wind was predominantly coming from \(-200°±20°\) between 0–9UTC and then changing rapidly to \(-90°±20°\) for the rest of the day. In August similar values as in July were observed and the reversal of the direction to the west sector occurred at about 18UTC. In September the variation of the wind direction was higher during night falling between 120° and 220°. The change of wind direction was not so clearly characterized but happened somewhere between 7–10UTC. During day the wind direction was from the east sector. At 18UTC the variation became higher with a tendency to shift to the west wind sector. Similar to September, October showed a high variation of wind direction during nighttime. The turn from the west wind sector to the east wind sector was not always very clear. After 12UTC the wind was primarily blowing from 80°–120°. Except for an outlier between 20UTC and 21UTC the wind blew from that sector for the rest of the day.

The distribution of the wind direction is expressed as the relative number of values for each sector. Values between 40° and 120° (defined by the author) belong to the up-valley wind sector while values between 200° and 320° belong to the down-valley wind sector. Values between 160° and 200° typically occur during Foehn events. The valley wind system can be seen quite well during all months. In July 59% of the wind was up-valley- and 33% down-valley. Only 3% occurred from the south. In August 42% were from the east sector and nearly the same (42%) from the west sector. 9% of the wind direction was associated with the south sector. In September the up-valley wind percentage increased to 54%, with only 28% occurring from west. Occurrence from the Foehn sector with 11% was the highest for all months. In October, the dominant east wind trend was continued and 53% were associated with it. 33% (nearly identical with
July) occurred from the west wind sector. 7% of the cases exhibited wind directions from the south. On average 52% of the daily wind was from the east while 34% was from the west. This results in a frequency-factor of 1.5 between west and east. The south sector is mainly depending on Foehn events, which can vary strongly depending on the season.

![Figure 3.2](image)

**Figure 3.2:** (A1-A4) monthly view of the wind speed (ff), (B1-B4) monthly view of the wind direction, (C1-C4) monthly view of the distribution of the wind direction. The red area is the standard error and the solid line the mean value over a month.

### 3.2 Footprint Analysis

For flux measurements the footprint analysis is an important tool to figure out the area where the flux information is mainly coming from. The footprint itself describes the spatial extension of a surface area under specific meteorological conditions and characteristics of the surrounding area. Especially in urban areas where the distribution of sinks and sources is more heterogeneous this information is crucial (Kljun et al.)
Karl et al. (2017) used a footprint model by Hsieh et al. (2000) for the field site of this thesis for the iNNAQS campaign 2015. The results are presented in Fig. 3.3. Footprint contour line intervals are 10%, from 10% (red) to 90% (dark blue). The dashed circles are 45m intervals around the flux tower. The dominant footprints are affected by the predominant wind sectors. Peaks are given between 270m – 320m at 60° and around 210°. The model shows that industrial emissions are not relevant in the footprint area (Karl et al. 2017). Especially, a thermal power station in the south west, which could have a significant impact on EnR is mostly outside of the most significant flux area. For the northeast sector, traffic at the Innrain street is very important as the footprint covers this area quite well. In summary, we can conclude that the footprint is representative for characteristic urban area in Innsbruck.

**Figure 3.3:** Footprint analysis by Karl et al. (2017). The isolines represent the relative amounts contributing to a turbulent flux signal (10% (red) to 90% (dark blue)). The inner scale represents the distance in meters from the measurement tower in the center. The outer scale is direction in degrees. The footprint analysis allows to exclude some kind of sources like those from industries as there is no relevant industrial sources in the footprint (taken from Karl et al. (2017)).
3.3 Traffic at the field site

Traffic is one of the most important sources for NO\textsubscript{x} emissions within an urban footprint. Another important source is domestic fuel and it is quite difficult to quantify the amount of these emissions. Traffic volumes are easier to quantify. This thesis relies on traffic count stations operated in the vicinity of at the field site by the City of Innsbruck and the Tyrolean government. The traffic was recorded as vehicles per hour in North–South directions and vice versa. The North–South direction was additionally differentiating between the number of heavy duty vehicles (HDV) and light duty vehicles (LDV). The traffic analysis allowed to identify appropriate weekday and weekend time windows with a sufficiently large number of values so that averaged diurnal traffic volumes could be calculated. A monthly view of traffic statistics is also calculated for further interpretation of NO\textsubscript{x} emissions.

Fig. 3.4 shows the results for diurnal traffic cycles splitted into a daily view on the left side and a monthly view on the right side. Shaded areas represent the standard error. It can be seen that the traffic amount is nearly equal from Monday through Thursday. Especially the daily course is identical, where traffic counts start to increase at 3UTC and exhibit a strong increase at 4UTC. At 3UTC public transport changes from night schedule to day schedule continuously shortening bus intervals up to 7UTC. The strong increase at 4UTC can be explained by the superposition of private transport. At 6UTC the values become constant with 540±16veh/h by 8UTC. After 8UTC a jump up to 694±12veh/h occurs. It may be confusing that this first peak is not during the typical rush hour (5–7UTC). The reason for this is caused by the summation of all counting directions, where traffic into the city during the rush hour is continuously superimposed by increasing traffic volumes in the opposite direction during the day. While directions into town have its peak indeed during the rush hour, the peak out of town occurs later. The overall peak is therefore seen between 8 and 10UTC. A local minimum can be seen at 12UTC at a level comparable with the morning plateau. Up to 15UTC the values are constantly increasing to 700±16veh/h which represents the daily maximum and corresponds well with the evening rush hour. After the rush hour, the values are declining fast until the end of the day. A short flat period can be seen between 20UTC and 21UTC. Night time values (0–3UTC) are around 30veh/h while daytime values are around 631±14veh/h.
On Friday, traffic count data are similar to values from Monday to Thursday up to 10UTC. The late morning peak is 723±32veh/h and therefore 29 vehicles higher than the Monday to Thursday average. The peak is also shifted by one hour. The most significant difference can be seen during the afternoon when the rush-hour peak is only 622±31veh/h, 78 vehicles smaller than on other weekdays. The reason is called “Friday effect” and is caused by a shorter workday for many people. Thus, the traffic load is more uniformly distributed during the afternoon. At 17UTC the Friday values correspond to other weekday values up to 20UTC. The weekend effect with higher traffic (~70veh/h) during night time occurs after 20UTC.

Saturday values lie between 80±3veh/h (4UTC) and 579±31veh/h (11UTC). Values between 0UTC and 4UTC are significantly higher than on weekdays with an average of 102±5veh/h, which is three times higher than on weekdays. The increase of the morning traffic is shifted by one hour because private transport is strongly influenced by working hours. A continuous increase happens up to 9UTC when the values peak at 570±24veh/h and are comparable with the late morning rush-hour values during working days. From 9UTC to 17UTC the values are varying between 500 and 600veh/h so they are nearly constant. After 17UTC the traffic volume is decreasing with the same weekend effect as observed on Friday. The daytime values of Saturday are on average 548±32veh/h, 83 vehicles smaller than during weekdays (e.g. Monday–Thursday).

On Sunday the values between 0UTC and 4UTC are nearly identical as on Saturday. The starting point of the morning increase is equal to Saturday but a constant traffic load window at 5–6UTC causes a shift by one hour before the daily maximum values are reached. From 9UTC to 17UTC the values are around 429±25veh/h and
values after 18UTC are similar to values weekdays (Monday to Thursday). Sunday has the minimal daily maximum with an averaged difference of 203veh/h. In general, the daily difference in traffic load between Sunday and weekday is about 34%.

As Friday and Saturday are different in their characteristics compared to the rest of the week the periods for weekday and weekend are defined as Monday to Thursday and Sunday.

In summer 2015 a construction area close to the field site led to a change in the traffic load. Up to the 6th of September 2015 this area was more difficult to pass. Especially HDV were re-routed to avoid the area. Additionally, during summer months (July–August) public transport operates with a different Saturday schedule due to summer holidays for students. In July, the daytime averaged value was 521±21veh/h. The typical morning peak did not occur. A local minimum occurred at 12UTC. The evening rush hour was not very dominant. In August, the daytime values were around 564±21veh/h. The late morning peak at 9UTC is clearly observed with a traffic column of 650±20veh/h. In the afternoon, the rush hour values are close to those observed for July. School started on the 7th of September and the construction area was also finished by then. The daytime average reached 640±24veh/h. In October, the diurnal course looked different compared to other months. The mean daytime value was 779±31veh/h. The morning peak was at 7UTC and the dip in traffic volume at about 12UTC was not very strong. The evening rush hour peak was therefore not very pronounced. The total values in October were between 10 and 220veh/h higher.

In general, it is noted that traffic loads showed a high variation on a monthly scale. Between July and October the traffic amount increased by around 50%. The diurnal cycles were also different for individual months.

### 3.4 Trend Analysis

The daily cycles of NO\textsubscript{x} and its compounds are plotted in Fig. 3.5. For completeness, the CO\textsubscript{2} concentrations are also illustrated because they are used in later sections. The red solid line represents the weekday mixing ratio (Mon-Thu) and the blue solid line the weekend (Sunday). The shaded area is representing one standard error. The mixing ratios of NO\textsubscript{x} and its compounds are given in parts per billion (ppb) and that of CO\textsubscript{2}
in parts per million (ppm). For weekdays 64 days are used for the statistical interpretation while just 16 Sundays are available for investigating weekends. Except for CO₂ all other gases show a significant weekday/weekend difference of their average day time concentrations.

3.4.1 Trends of Nitric Oxide

For the weekday window the concentration range of NO varied from \(0.2\pm0.2\) ppb around midnight up to \(18.0\pm2.3\) ppb at 6UTC. The lowest values occurred during 0 and 3UTC while the highest values were measured around 6UTC. Between 10-16UTC the values fell close to \(-5\pm1\) ppb. After 16UTC NO mixing ratios declined again. On weekends, the daily trend was flatter. The lowest values were at the limit of detection (-0.1±0.2 ppb\(^1\)) during night. The highest value with \(3.0\pm0.9\) ppb was observed at 7:30UTC. After the morning peak NO concentrations were continuously decreasing until 14:30UTC when they stagnated for 1.5 hours. Another increase was observed at 19UTC. Between 0UTC and 3UTC NO concentrations for weekends were higher than for weekdays. This can be explained by more traffic on Sunday night (party effect).

In general, the diurnal course of NO mixing ratios is strongly influenced by traffic, meteorology and photochemical processes (Villányi et al. 2010). The superposition of the effects lead to a typical daily cycle shown in Fig. 3.5. The point when NO concentrations increase corresponds to an increase in traffic volume. The morning peak especially on weekdays, however, cannot be explained by traffic load alone. A weak nocturnal capping inversion layer may amplify increasing emissions leading to a pronounced concentration peak until about 6UTC. Subsequently entrainment and photochemical repartitioning lead to decreasing mixing ratios starting at about 10UTC and reaching a local minimum at about 18UTC. During daytime, NO oxidation is compensated by the photolysis of NO\(_2\). The rush hour peak during the evening was therefore completely hidden which is caused by a combination of fast conversion and a well-mixed boundary layer. After 16UTC the weekday mixing ratio strongly declined which matched traffic loads. An increase of the values can be seen on weekend and weekdays at 18UTC. There are several possible reasons. At sunset a low nocturnal inversion layer starts developing and finally results in an increase of the concentration as traffic loads

\(^1\) negative concentrations are physically not possible but occur by zero correction as the mean values of the calibration measurements are subtracted;
are still high. Another possible explanation could be an increase in domestic fuel use during evenings. On weekends the concentration was increasing up to 8UTC with no dominant peak compared to weekdays. Due to a later start of the traffic increase the inversion layer had no effect on the concentrations values anymore. After 8UTC NO concentrations were continuously declining up to midnight.

Another important factor that impacts diurnal NO concentrations is caused by the conversion rate between NO and NO\textsubscript{2} (Han et al. 2011). This can provide an additional explanation why NO and NO\textsubscript{2} are not always in steady state.

### 3.4.2 Trends of Nitrogen Dioxide

Weekday nitrogen dioxide varied between 6.4±0.4ppb (23:30UTC) and 20.3±0.8ppb (5:30UTC). Local minima occurred during night and during noon. On weekends the extrema of NO\textsubscript{2} mixing ratios were 4.4±0.5ppb (11:30UTC) and 11.0±1.8ppb (18:30UTC) respectively. The daytime minimum of around 5ppb was observed between 10UTC and 13UTC. The morning peak at working days is correlating with the traffic volume but absolute values cannot be explained by the traffic alone. At 6UTC a decrease of NO\textsubscript{2} occurred up to 10UTC. Reasons may be the same as described in section 3.4.1. Between 10 – 16UTC the values were continuously growing. At 18UTC a depression of ~2ppb was observed. A similar decrease could also be seen for NO. The local peak at about 20UTC corresponded to an increase of NO concentrations at this time. A detailed explanation for this pattern is given in the subsection 3.4.1. Later at night NO\textsubscript{2} mixing ratios were drastically declining to a minimum.

### 3.4.3 Trends of Carbon Dioxide

Carbon dioxide is used later for the EnR approach and therefor shortly presented here. CO\textsubscript{2} showed a diurnal cycle with a minimum peak for weekdays of 400.9±1.5ppm (18UTC) and a maximum of 412.7±4.7ppm (10UTC). This was a daily variation of just 3% (11.8ppm). For weekends the minimum was 398.9±3.9ppm (21UTC) and the highest mixing ratio 415.6±10.0ppm (9:30UTC). Overall this resulted in a daily variation of 4% (16.6ppm). The diurnal course corresponds to those of other cities (Moore and Jacobson 2015, Rice and Bostrom 2011) although the amplitudes for both periods were smaller. In general, the variation of CO\textsubscript{2} was smaller during day than during night.
caused by turbulent mixing during daytime. Increase and decrease of the daily concentration cycle can be described by a superposition of biological activities like photosynthesis and respiration and changes in the PBL height (Rice and Bostrom 2011). Especially between 2UTC and 16UTC CO$_2$ values are higher on weekends what may be mainly caused by a smaller sample size as the amplitude is generally bigger on Sundays. Applying a hypothesis test found no evidence of a significant weekday/weekend effect.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure3.5.png}
\caption{(A-D) daily averaged cycle of specific pollutants (A: NO, B: NO$_x$, C: NO$_2$, D: CO$_2$). The red solid line represents the values for weekdays and the blue one for weekends. The shaded area is the standard error for each interval.}
\end{figure}

\section*{3.4.4 Wind directional dependency of mixing ratios}

In the following concentration levels are analysed by the wind direction (see Fig. 3.6). The median concentration for each species (black solid line) was calculated for individual 10° intervals. The error bounds (red shaded area) are calculated as described previously. Overall 5376 30min averages were available for this analysis. The grey dots represent the raw data.

Averaged NO values vary between the limit of detection (-0.1ppb - more details are found on page 50) and 4.6ppb. Higher values are observed in the east sector with an average of 2.5±0.9ppb, while the west sector has values of 0.5±0.6ppb. During Foehn events the values dropped to 0.4±0.8ppb. A local maximum occurred at 120° corresponding to the overall maximum value (4.9±0.7ppb). At 210° a maximum value of 2.5±1.0ppb was observed. On average the NO concentrations of valley up winds were 2.6 times higher than those for valley down winds. Foehn events had the lowest mixing ratios due to a well diluted boundary layer. The huge difference between east and west is caused because NO values continuously decreased during the night when mainly valley downwind conditions persist.
NO\textsubscript{2} concentrations show values between 4.2ppb and 13.1ppb. The lowest values were observed in the Foehn sector at 180° during Foehn events. A well-mixed boundary layer caused this local minimum. Average concentrations for the east sector were about 11.7±0.7ppb and 9.6±0.6ppb for the west sector. The significance test (see Appendix) shows that there is a statistically significant difference between both sectors. Values from the east sector were on average 21% higher than from west sector.

![Figure 3.6](image)

**Figure 3.6:** Wind dependency for NO (A) and NO\textsubscript{2} (B). The distribution of the data is affected by the thermally driven valley wind system and Foehn events.

### 3.5 Evaluation of the enhancement ratio approach

As outlined in chapter 2.4, we will use the enhancement ratio approach to distil emission factors, which are not influenced by confounding factors that typically impact mean concentration ratios. The EnR approach will be evaluated based on measured flux ratios. The flux ratio is calculated by dividing the flux of NO\textsubscript{x} by the flux of CO\textsubscript{2} and is given as

\[
FR_{Y/X} = \frac{(w'Y')}{(w'X')} \tag{3.1}
\]

specifically, as

\[
FR_{\text{NO}_x/\text{CO}_2} = \frac{(w'\text{NO}_x')}{(w'\text{CO}_2')} \tag{3.2}
\]

Thereby it will be verified to what extent the following relation is true:

\[
FR_{\text{NO}_x/\text{CO}_2} \propto \text{EnR}_{\text{NO}_x/\text{CO}_2} \rightarrow \frac{(w'\text{NO}_x')}{(w'\text{CO}_2')} \propto \frac{(\text{NO}_x'\text{CO}_2')}{(\text{CO}_2'\text{CO}_2')} \tag{3.3}
\]
3.5.1 Trends in enhancement and flux ratios

The results are shown in Fig. 3.7 where EnR and FR are plotted for weekdays (A) and weekends (B). The blue bar represents the flux ratio and the red bar the enhancement ratio for each hour. The grey interval is one standard deviation. The magenta line is the calculated ratio for daily traffic EnRs with the mean as solid line and the green area and line is equivalent to the residential combustion ratio (Karl et al. 2017).

A daily variation for EnR and FR on weekdays is obvious. During the night and in the morning hours the EnR and FR differ most with larger amplitudes for the FR. In general, the flux ratio is higher under stable atmospheric stratification. The lowest value of the weekday EnR is 3.6E-4±3.7E-4 (23UTC) and the highest value is 3.6E-3±1.0E-3 (15UTC) corresponding to the evening rush hour. Weekday flux ratios have a minimum of 7.2E-4±7.0E-4 (2UTC) and a maximum of 3.9E-3±1.3E-3 (13UTC). On average the flux ratio is twice as high during night than the enhancement ratio but the EnR is near the calculated residential combustion ratio. The over- and underestimation between EnR and FR is between +3% and -78%. Better agreement can be found during the daytime window between 14-16UTC. It’s the time when well developed turbulence leads to a well-mixed boundary layer. The standard deviation for both ratios is about 1.0E-3.

On weekend the values for both ratios are smaller. The minimum for EnRs is 2.0E-4±1.4E-4 (23UTC) and the maximum 2.5E-3±1.1E-3 (15UTC). The flux ratio is between 4% and 289% higher. The highest value occurs at 4UTC when the traffic load was lowest. A clear reason for that cannot be found but a large standard error signalizes strong variations at that time during sunrise. The best correlation between EnR and FR is found between 14–15UTC and the weakest during morning hours. The lowest flux ratio was 5.3E-4±3.2E-4 (2UTC) and the maximum ratio was 3.2E-3±1.1E-3. While the minimum values lie within predicted residential combustion ratios, the maximum ratios never reached the calculated traffic ratio. The flux ratio was nearly constant between 8UTC and 16UTC, the EnR was constant between 8 – 11UTC and 13 – 17UTC.

When comparing the weekday flux ratios and the weekday enhancement ratios it is clear that both ratios are affected by traffic (especially during daytime) but it is also obvious that the values show some differences depending on the time of day. One explanation could be that the flux ratio is more sensitive to mixing with background
air during stable conditions. This could explain a local minimum at 8UTC for weekday flux ratios. A very low weak nocturnal capping inversion layer which is removed within hours after sunrise separates the high NO\textsubscript{x} concentrated ground-based air from lower concentrated upper air. After mixing the gradients become lower and therefore the vertical mixing reduces as observed in the morning hours. Yokelson et al. (2013) described this phenomenon for EnRs. The EnR seems to be more sensitive on wind speed and stability. Especially in the morning hours between 3UTC and 10UTC the values are significantly lower than the flux ratio but therefore relatively constant. When stability decreases and wind speed increases the EnR approaches values near the flux ratio.

The weekend flux ratio does not show a minimum around 8UTC. This may be caused by a later increase of traffic. The gradients are not as high as on weekdays and therefore the effect is damped. The wind speed has not a significant influence on the flux ratio as the values become nearly constant at 8UTC which corresponds to the Sunday traffic load quite well.

**Figure 3.7:** The boxplots depict the EnR (A) and the FR (B). The grey lines are one standard error. The green line (with standard error) represents the calculated combustion ratio, the magenta line (with standard error) is the calculated traffic ratio.
It can be concluded that the daytime development of both ratios is the result of overlapping processes mainly the development of traffic load and changes caused by a continuously changing footprint. During the day domestic fuel is not influencing the EnR as dominantly as during the night.

### 3.5.2 Regression analysis

A powerful statistical method to analyse the relationship between two interrelated variables is the use of regression analysis (Goldberg and Cho 2004). In the following the proportionality between the EnR and the FR is analysed.

The results are shown as a scatter plot for weekday (A) and weekend (B) in Fig. 3.8. The enhancement ratio (y-axis) is plotted against the flux ratio (x-axis). The red and blue solid lines are the linear regression lines. The dashed grey line is the median and the dots are the actual data. The colour of the dots represents the daytime according to the colour bar from dark blue (0UTC) to yellow (24UTC). For weekdays 992 (of 3072 = 32%) data points were used to calculate the regression line, while just 230 (of 768 = 30%) data points were available for the weekend regression line.

**Figure 3.8**: Scatter plot between the flux ratio and the enhancement ratio for weekdays (A) and weekend (B). The fitting line shows that higher flux ratios tend to be underestimated by the enhancement ratio.

The data points for both time windows cluster around the median what is expected when comparing with Fig. 3.7. The ratios are positively correlated. Data points below the median are scattering more. Higher values of FR correlate with lower values of
EnR which happens mainly during night time and in the morning as well as during Foehn events. As this scatter is obvious for both methods, it can be concluded that stability must have a great influence. The coefficient of determination ($R^2$) for weekdays is 0.57 and for weekends 0.66. The fitting equation for weekdays is given as

$$f(x) = 0.69 \cdot x + 6.00 \times 10^{-4}$$

where $f(x)$ is the EnR and $x$ the flux ratio. The slope is 0.69. The offset is $6.00 \times 10^{-4}$. The fitting equation for weekend is given as

$$f(x) = 0.73 \cdot x + 9.85 \times 10^{-5}.$$  

The slope is larger than for weekdays. It should be noted, though, that there are fewer data in the statistical analysis. Overall it can be seen that flux ratios tended to be underestimated. An longer campaign should help obtain more accurate results as more data would be available for the regression analysis. This analysis shows, that the method of enhancement ratios and the method of flux ratios yield comparable results within 30%. During daytime (9-17UTC) conditions the relative mean difference between both methods is on the order of 15%.

### 3.6 Enhancement Ratio Trend Analysis

In the following part trends of EnRs are analysed in more detail. Different time windows are investigated to better understand the traffic load influence as well as micrometeorological effects.

#### 3.6.1 Weekday/ Weekend Effect

In Fig. 3.9 the results of different EnRs are plotted as “boxplots” for weekdays (A) and weekends (B). For comparison, they are also overlaid in panel (C). The shadow area in C is one standard deviation. The EnR on weekends were between 0 and 172% lower than on weekdays. During night (0-3UTC) the weekend EnR was about 38% higher than the weekday EnR. This can be simply explained by the fact that traffic activity is higher on Sunday night due to the “weekend party effect”. During daytime (9-17UTC) the difference between the weekend and weekday ratio was about 32%. This correlates perfectly with the 33% lower traffic load during the same time window.
Overall it can be seen that the biggest difference between the time periods was during the morning window. The weekend/weekday difference disappears in the evening beginning at 17UTC. In the morning, the 68% lower weekend ratio is likely caused by a 69% reduced traffic load.

Figure 3.9: (A) shows the weekday EnR as boxplot with the median as black filled circle, (B) shows the weekend EnR. Mean absolute values with one standard error (shaded area) of both ratios are overlapped in panel C.

Overall the weekday/weekend effect is depending on the time of day and is mainly driven by the traffic volume. The biggest change was observed between 3-15UTC, when the biggest difference in traffic volume occurred. After 15UTC the weekend effect vanished completely. The “weekend party effect” resulted in a short increase of the EnR between 0-1UTC on weekends.

### 3.6.2 The monthly view

A monthly view during the campaign gives the opportunity to investigate the seasonal variability of EnRs. Different traffic amount and speed behaviours of vehicles, as well as seasonal cycles of vegetation can potentially influence the composition of the EnRs as these effects change the distribution and weighting of sources and sinks. The consumption of domestic fuel is additionally affected by the use of heating systems during “cold” months.

The results are shown in Fig. 3.10. The EnRs are plotted for July–October, averaged for every hour. The left plots (red coloured) show the weekday EnRs and the
right plots (blue coloured) the weekend EnRs. The number of selected data varies between 470 (=54% of 864) and 751 (=87% of 864) for weekdays and between 111 (=49% of 240) and 131 (=91% of 144) for weekends.

The EnRs show a high variability between individual months exhibiting large standard deviations. The daily maximum values for weekdays lie between 4.7E-3±4.5E-4 and 3.2E-3±5.3E-4 and occur during daytime. There is a decreasing tendency from July to October. Night values range between 2.4E-4±2.5E-4 to 5.9E-4±2.7E-4 with a decreasing tendency from October to July which is inverse to the maxima. Daily courses are month dependent, especially during the morning hours (between 3UTC and 10UTC) EnRs differ significantly. While in July and August the values were nearly constant around 1E-4 and 1.3E-4. In September the morning EnRs were around 2.5E-4. October showed similar values compared to September, exhibiting a sudden jump after 7UTC. Traffic load cannot describe this variability sufficiently and other effects may have caused this change. Therefore, further investigations would be necessary to provide an explanation for this behaviour. Especially a ground based inversion layer may have played a greater influence but vegetation and the construction site near the field site might have also played a role as discussed earlier. During daytime the EnR showed their typical course but also exhibiting a high variability. The daily maximum was reached between 15UTC and 16UTC. Except for October all months reached the calculated daily traffic ratio. One reason for this could be an increase in domestic fuel burning which is more dominant in autumn due to heating systems.

For weekends, the statistical significance was extremely weak. Especially in August the interquartile range for morning hours was extremely high (up to 7 times of the median). The maximum values were between 2.1E-3±5.3E-4 (October) up to 3.6E-3±8.8E-4 (July). August and September had nearly the same daily maximum values around 2.5E-3. This was close to the daily weekend average of the whole campaign. On weekends, enhancement ratios approached the calculated traffic ratio only in July but not during the other months. The values during mornings ranged from around 1.5E-4 (July) to 6.0E-5 (October). This trend was also seen for weekdays. The strong increase in the morning varied between 8UTC (September) to 13UTC (August).
Figure 3.10: Monthly view (July-October) of the EnR for weekdays (A, C, E, G) and weekends (B, D, F, H) as boxplots with the median as black filled circle. The green line is the calculated combustion ratio and the magenta line represents the calculated traffic ratio. The shaded area is one standard error.

3.6.3 Comparison between 2015 and 2016

Another short campaign with a similar setup took place in 2016. It started on April, 6th and ended on June, 27th with 83 measurement days. Compared to the campaign in 2015 the calibration was fully operational with Zero Air and Span correction. The campaign in 2016 allows to compare the EnR values with 2015 and estimate the ratios during a different season. One significant change between 2015 and 2016 was that the construction area was not influencing the measurement site anymore. The data processing procedure for 2016 was identical to the one as used in 2015. The EnRs are plotted for the entire campaign in 2016. Weekdays and weekend are used as defined previously. Additionally, one needs to be aware that the seasons considered for the two
consecutive years are different. While the 2015 campaign was dominated by summer and autumn conditions, the 2016 campaign 2016 was characterized by springtime conditions.

The results for 2016 are shown in Fig. 3.11 where weekday data plotted on the left side (red) and weekend data on the right side (blue). The shaded areas are defined as before. The daily course of the weekday EnR was strongly influenced by traffic load. Nighttime EnRs were correlating well with the calculated residential combustion ratio from 2015. During the morning hours the EnR were increasing up to 1.7E-3 which is close to the 2.0E-3 of 2015. The local minimum at 8UTC was more dominant in 2016. During daytime ratios were evolving differently compared to 2015. The daily maximum of 2.6E-3±6.2E-4 was reached at 14UTC and was 27% smaller than during the 2015 campaign. While the values during daytime (4 – 17UTC) were about 20% smaller, the values during nighttime (18 - 3UTC) were 14% higher. Traffic data were not available for the specific period what makes a precise investigation more difficult. The daytime values were comparable with October ratios.

The weekend EnRs were between 2.45E-4±3.76E-4 and 2.00E-3±6.40E-4 which makes the minimum 24% higher and the maximum 20% smaller than in 2015. In general, the EnR are more constant during daytime compared to 2015. A stable EnR suggests that the ensemble of sinks and sources was not changing as much. The over- or underestimation was fluctuating during the day (e.g. between -46% (4UTC) and +209% (23UTC)). Especially between 9UTC and 11UTC the EnR was higher than the year before.

The qualitative view of the different seasons showed an interannual variation of the EnR. The diurnal courses were similar but the quantities differed. The daytime weekday ratios in 2016 did not reach those in 2015. Probably a different traffic to domestic residential burning ratio could be one reason for these differences. A weekday/weekend effect was also evident in 2016 exhibiting a 24% smaller weekend ratio. In 2015 this value was 33%. Afternoon values on weekdays exhibit little variability and are nearly year independent. This suggests that atmospheric stability plays an important role for the evaluation of enhancement ratios.
Figure 3.11: Comparison of the campaign 2015 and 2016 for weekdays (A) and weekends (B). The error bars show a high variation for both windows. The values of 2016 are smaller than those of the previews campaign and do not reach the calculated traffic EnRs of 2015.

3.7 Emission Ratio modelling

EnR represent the ensemble ratio of different types of sources. Within the flux footprint two main sources of NO\textsubscript{x} were classified. A minimization routine is being used to unmix this two end-members and calculate the activity factors for traffic and domestic fuel. The result is shown in Fig. 3.12. The left figure represents the results for weekday EnRs and the right one for the weekend EnRs. The values are plotted for every hour per day. The solid black line with error bars is the true EnRs while the dashed red line is the modelled EnRs. The dotted grey line represents the traffic/domestic activity factor. The bounds for the minimization routine are taken from reported emission factors described in Karl et al. (2017). The weighting factors of the emission factors are applied according to Haun (2014) and Stanzel et al. (1995).

It can be seen that the emission ratio model used by Karl et al. (2017) fits the true measurements quite well on weekdays (A). There are some limitations between 10UTC and 16UTC. The activity factors for traffic vary between 12% (1UTC9) and 98%
(12UTC). Lower values occur during night while the highest ones are during daytime. During night time the traffic activity factor is around 15% and during day 72%. In the morning hours during rush hour the traffic activity factor is around 50%. The calculated traffic activity factor is 3.4E-3 and for domestic fuel 1.1E-4.

For weekends the results are shown on the right panel (B). Between 12UTC and 17UTC the observed and modelled ratios are agreeing quite well. The composition of the domestic and the traffic EnR cannot describe values above 2.0E-3 due to boundary restrictions. Traffic activity factors range from 3% (23UTC) up to 97% (12UTC and 18UTC). The diurnal averaged traffic activity factor is 56% and nearly equal to the weekday one. The night time traffic activity factor is about 35% and about twice the value for weekdays. This is caused by higher traffic loads on Sunday night. The calculated traffic emission ratio is about 2.0E-3 and the domestic one 1.1E-4.

Comparing the calculated EnRs for weekdays and weekends results in a 70% higher traffic emission ratio for weekdays while the domestic fuel emission ratio is nearly equal for both scenarios. This is not surprising as domestic fuel use is not so much affected by the weekday/weekend effect, especially during summer months where often just water heating systems are operating. Taking the ratio between the traffic load for weekdays and weekends suggests that there was 54% more traffic on weekdays.

**Figure 3.12:** The applied emission ratio model for weekdays (A) and weekends (B) calculated the ratios between the two main sources: traffic load and domestic fuel use. The red dashed line represents the modelled emission ratio, while the grey dotted line represents the traffic activity factor.
Chapter 4

4 Conclusion

The EnR approach defined in section 2.4 was applied to an urban area within the Alps. Correlation between NO$_x$/CO$_2$ flux ratios and NO$_x$/CO$_2$ EnR suggests that both methods work well during the day when turbulence is well-developed. During the night and evening the EnR approach yielded lower values than measured flux ratios and scatter increased. Aubinet et al. (2003) discussed the nocturnal applicability of micro-meteorological flux measurements extensively while at the moment there is no such study (2017) relating this question to EnRs. It is suggested that the tools commonly used for flux measurements should also be applied to turbulent EnR data. This includes common QAQC and footprint analysis. Especially the steady state test criteria, criteria on developed turbulence and the signal to noise analysis are important to obtain useful EnRs. Yokelson et al. (2013) discussed the sensitivity of EnR with respect to changing background values, which could pose one challenge when obtaining EnRs in a nocturnal boundary inversion layer, where turbulence is low and often intermittent. In general, it could be shown that the EnR approach is an equivalent method compared to emission ratio calculations based on measured turbulent fluxes.

The daily EnRs are influenced by two main pollution sources in Innsbruck. The footprint analysis applied by Karl et al. (2017) for the iNNAQs campaign 2015 localized the dominant area of interest. In that area, industrial emissions could be excluded and traffic load and domestic fuel consumption dominate the emissions of NO$_x$ and CO$_2$. This fact resulted in a pronounced weekday/weekend effect. EnRs were in general lower on weekends than on weekdays which can be explained by traffic volumes. A prominent diurnal cycle for EnRs was observed, which was explained by superimposed effects like varying emissions of the main pollution sources and meteorology. The calculated daily
maximuns of weekday EnRs were similar to other studies (Carslaw et al. (2011), Carslaw et al. (2013), Ammoura et al. (2014)). Maximum EnR values, observed during this study fell close to the Euro Diesel emission classes 4-5, suggesting that a large fraction of NO\textsubscript{x} originated from Diesel driven cars and trucks. Due to a construction site in the vicinity of the measurement tower during the 2015 campaign, heavy duty vehicles were re-routed to a large extent and played a small role within the flux footprint. In general, the area was therefore mostly dominated by passenger cars, light duty transport vehicles and busses for public transport, comprising a large amount of Diesel driven vehicles. Diesel driven busses are known to emit a higher NO\textsubscript{x}/CO\textsubscript{2} ratio, but typically account for just 5% compared to the number of passenger cars. Yet, in urban centres, public transport by busses often clusters and comprises a larger fraction than the Nationwide fleet average. It can therefore play a locally important contribution to NO\textsubscript{x} emissions. On weekends EnR ratios changed according to absolute traffic load values and comparison between weekdays and weekends could be explained by this change quite well.

In general, traffic can explain 50% of the observed NO\textsubscript{x}/CO\textsubscript{2} emission ratios averaged over the course of the day. While traffic dominates NO\textsubscript{x} emissions during the day, the measurements suggest that domestic fuel can have a significant impact on local emissions, especially when daily emissions are investigated. It is noted that emissions from residential combustion units are poorly constrained. During daytime traffic explains up to 90% of NO\textsubscript{x} emissions and accounts for a dominant portion. On the monthly basis it could be shown that the EnRs show a high variation. They decreased from high values in July to lower values in October. Probably multiple effects contribute to that result. A seasonal variation in domestic fuel use and traffic volumes must be responsible for these changes. Additionally, driving behaviour which vary between individual months may also affect these values. Different studies showed that emissions are generally increasing with decreasing driving speed up to a threshold. It must be noted that higher values of EnRs occurred in summer when traffic within the footprint was lower. This supports the theory that sources between domestic fuel and traffic load are not only changing over the day but also seasonally. For any further interpretation, a more in-depth investigation of these variations is necessary. Long-term measurements over a year should help to visualize seasonal variations and should help to improve data quality as the amount of available data increases. Additionally, measurements
during the winter season which was not covered in 2015 would also be necessary to see to what extent the weighting factors between traffic and domestic fuel are changing.

Comparison of the EnRs between 2015 and 2016 showed a different daily maximum. An explanation for this finding could be the different seasons covered by the measurements as was previously discussed. This is something which needs further investigation. Especially the seasonal trend is not fully understood.

In order to better understand the formation processes of NO$_x$, top-down measurements described in this thesis should be compared with bottom-up approaches including measurements at the street level. This would also help to improve the understanding of the chemical processes in street canyons and the repartitioning of NO and NO$_2$. In-situ measurements are a promising way to evaluate emission models because the pollutants are observed almost immediately after being emitted.

It is concluded that EnRs can be a valuable approach for evaluating up scaled urban emission ratios of pollutants. Future measurements should be conducted on a long-term basis and combined with bottom-up emission models. This would lead to an improved accuracy of emission inventories.
5 Bibliography


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Appendix

All data – used in this section – are plotted or calculated by routines programmed in Matlab R2015b (v8.6). Gaps are generally filled with NaNs. Error bounds are calculated by the widely used standard error equation

$$\sigma_{err} = \frac{\sigma}{\sqrt{N}}$$

where \(\sigma\) is the standard deviation for each interval and \(N\) the sample size of the dataset. Significance test were calculated as described in Student (1908) and applied according to the Matlab help where \(h\) is the result of hypothesis decision, \(p\) the \(p\)-value and \(ci\) the confidence interval at a 5\% significance level. Averaged values are calculated with the median function except where otherwise specified.

Significance test for NO\(_x\), NO\(_2\), NO\(_x\)

In Table A.1 NO\(_x\) data are listed as 30min values used for figures in section 3.3. Weekdays (Mon-Thu) and weekends (Sun) are separately calculated and a t-test was performed for significance analysis. Concentration values are given in ppb. Time is in UTC.

### Table A.1: Hourly concentration levels for weekdays/weekends and significance test

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<th>NO(_2)</th>
<th>NO(_x)</th>
<th>NO(_2)</th>
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<td>wS(^5)</td>
<td>wd(^5)</td>
<td>wS(^5)</td>
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\(^{5}\) \(h\) is the result of hypothesis decision, \(p\) the \(p\)-value and \(ci\) the confidence interval at a 5\% significance level. Averaged values are calculated with the median function except where otherwise specified.
Tyrolean government. The data are time corrected from local time to UTC. The traffic is measured at the crossroad Innrain/Anichstreet next to the measurement tower by the Traffic analysis

<table>
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<th>Fri</th>
<th>Sat</th>
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<td>7</td>
<td>10</td>
<td>13</td>
<td>16</td>
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2) mean concentration values for 30min interval in ppb defined as Mon-Thur
3) mean concentration values for 30min interval in ppb defined as Sunday
4) hypothesis test (t-test) with h: w 0.01
5) standard error in vehicles/h defined as median of traffic volume in vehicles/h
6) traffic analysis

Traffic analysis

Table A2. Traffic load data on a daily view from Mon-Sun and as averaged values for Mon-Thur. These values are used in section 3.3. The data are recorded at the crossroad Innrain/Anichstreet next to the measurement tower by the Tyrolean government. The data are time corrected from local time to UTC. The traffic load is given as vehicles per hour.

Table A2: Hourly traffic load values on a daily view and a weekday view (Mon-Thur)

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<th>Sat</th>
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</table>

1) medium of traffic volume in vehicles/h
2) standard distribution of the traffic volume in vehicles/h
3) standard error in vehicles/h defined as mean (σ) where σ is standard deviation and N sample size
4) sample size
Wind direction dependency of NO, NO₂ and NOₓ concentrations

In Table A.3 NOₓ and its compounds data are listed as 30min values used for figures in section 3.3. Concentration values are given in ppb. the wind direction in degree. The number of valid values varies due to the steady state criteria.

<table>
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<th>Wind direction (°)</th>
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<th>NO std (ppb)</th>
<th>NO₂ (ppb)</th>
<th>NO₂ std (ppb)</th>
<th>NOₓ (ppb)</th>
<th>NOₓ std (ppb)</th>
<th>Number of values</th>
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<tr>
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<td>54</td>
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<td>0.61</td>
<td>10.04</td>
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<td>330</td>
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<td>0.66</td>
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<td>1.42</td>
<td>41</td>
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<td>0.91</td>
<td>30</td>
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<tr>
<td>350</td>
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<td>0.39</td>
<td>9.07</td>
<td>0.63</td>
<td>10.04</td>
<td>0.92</td>
<td>74</td>
</tr>
</tbody>
</table>

1) wind direction in degree
2) median of concentration in ppb for 10° wind direction interval
3) standard error in ppb defined as \( \frac{s}{\sqrt{N}} \) where \( s \) is standard deviation and \( N \) sample size

In Table A.4 the traffic load data are listed on a monthly view from July to October. These values are used in section 3.3. The data are recorded at the crossroad Innrain/Anichstreet next to the measurement tower by the Tyrolean government. The data are time corrected from local time to UTC. The traffic load is given as vehicles per hour.
Table A.4: Hourly traffic load values on a monthly view

<table>
<thead>
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<th>hour</th>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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<th>10</th>
<th>11</th>
<th>12</th>
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<th>19</th>
<th>20</th>
<th>21</th>
<th>22</th>
<th>23</th>
</tr>
</thead>
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<td>50.0</td>
<td>41.0</td>
<td>39.6</td>
<td>45.0</td>
<td>79.0</td>
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<td>74.0</td>
<td>0.0</td>
<td>74.0</td>
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<td>49.0</td>
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<td>39.6</td>
<td>45.0</td>
<td>50.0</td>
<td>30.0</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>30.0</td>
<td>30.0</td>
<td>45.0</td>
<td>70.0</td>
<td>30.0</td>
<td>47.0</td>
<td>27.0</td>
<td>49.0</td>
<td>54.0</td>
<td>59.0</td>
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<td>45.0</td>
<td>0.0</td>
<td>30.0</td>
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</table>

Enhancement Ratio, Flux Ratio

In Table A.5 the median and standard deviation of the EnRs and FRs are plotted for weekdays and weekends. Data are resolved as 1h-values. The data are used in section 3.5.1. EnRs and FRs are given in ppb/ppb/week. Time is in UTC.

Table A.5: Comparison between enhancement ratio and flux ratio for weekdays and weekends

<table>
<thead>
<tr>
<th>hour</th>
<th>weekday</th>
<th>EnR</th>
<th>EnR std</th>
<th>FR</th>
<th>FR std</th>
<th>weekend</th>
<th>EnR</th>
<th>EnR std</th>
<th>FR</th>
<th>FR std</th>
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</thead>
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<td>4.00E</td>
<td>4.00E</td>
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</table>

Enhancement Ratios – weekend/weekday

In Table A.6 the median and standard deviation of the EnRs are plotted for weekdays and weekends. Data are resolved as 1h-values. The data are used in section 3.6.1. EnRs are given in ppb/ppb/week. Time is in UTC.
Enhancement Ratios - monthly view

In Table A.7 the median of the EnRs are plotted for each separate month during the campaign for weekdays and weekends. Data are resolved as 1h-values. The data are used in section 3.6.2. EnRs are given in ppb/ppb. Tim is in UTC

Table A.7: Hourly EnRs on a monthly view for weekdays and weekends

<table>
<thead>
<tr>
<th>Weekday</th>
<th>July ¹⁾</th>
<th>August ¹⁾</th>
<th>September ¹⁾</th>
<th>October ¹⁾</th>
<th>July ¹⁾</th>
<th>August ¹⁾</th>
<th>September ¹⁾</th>
<th>October ¹⁾</th>
</tr>
</thead>
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<td>3.10E-04</td>
<td>2.90E-04</td>
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<td>4.50E-04</td>
<td>5.10E-04</td>
<td>1.12E-03</td>
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<tr>
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<td>2.95E-04</td>
<td>2.58E-04</td>
<td>0.95E-04</td>
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<td>7.00E-04</td>
<td>5.31E-04</td>
<td>7.35E-04</td>
</tr>
<tr>
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<td>5.10E-04</td>
<td>7.35E-04</td>
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<td>1.11E-04</td>
<td>7.35E-04</td>
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<tr>
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<td>2.10E-03</td>
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<td>1.12E-03</td>
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<td>5.49E-04</td>
<td>9.70E-04</td>
<td>7.35E-04</td>
</tr>
</tbody>
</table>

¹⁾ median of EnR in ppb/ppb
Enhancement Ratio 2015 and 2016

In Table A.8 the median and standard deviation of the EnRs 2015 and 2016 are plotted for weekdays and weekends. Data are resolved as 1h-values. The data are used in section 3.6.3. EnRs and FRs are given in ppb/ppb. Time is in UTC.

<table>
<thead>
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<th>hour</th>
<th>weekday</th>
<th></th>
<th>weekend</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>EnRmed(a)</td>
<td>EnRstd(a)</td>
<td>EnRmed(b)</td>
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<td>5.49E-04</td>
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<td>1.83E-03</td>
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<td>1.64E-03</td>
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<td>2.51E-03</td>
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</tr>
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<td>5.78E-04</td>
<td>6.09E-04</td>
</tr>
</tbody>
</table>

(a) median in ppb/ppb
(b) standard distribution in ppb/ppb

Emission ratio modelling

In Table A.9 the EnRs of the measurement and the model are listed. The traffic activity factor describes how much of the modelled value can be described by traffic. The rest is related to domestic fuel use. EnRs are in ppb/ppb and the traffic activity factor is in %. Time is in UTC.
Table A.9: Comparing modelled and measured enhancement ratios

<table>
<thead>
<tr>
<th>hour</th>
<th>EnR(_{\text{calc}})^a</th>
<th>EnR(_{\text{meas}})^b</th>
<th>traff. act. factor(^c)</th>
<th>EnR(_{\text{calc}})^a</th>
<th>EnR(_{\text{meas}})^b</th>
<th>traff. act. factor(^c)</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>4.58E-04</td>
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</tr>
<tr>
<td>3</td>
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<td>13%</td>
<td>1.94E-04</td>
<td>3.05E-04</td>
<td>31%</td>
</tr>
<tr>
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<td>1.61E-04</td>
<td>4.90E-04</td>
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</tr>
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<td>65%</td>
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</tr>
</tbody>
</table>

\(^a\) measured EnR in ppb/ppb
\(^b\) calculated EnR in ppb/ppb
\(^c\) ratio between traffic activity and domestic activity in %

**Absolute NO\(_x\) and CO\(_2\) fluxes**

In Fig. A.1 the daily absolute fluxes (in ppb m\(^{-2}\)s\(^{-1}\)) for NO\(_x\) are plotted for each month of the campaign. In Fig. A.2 the daily absolute fluxes (in ppm m\(^{-2}\)s\(^{-1}\)) for CO\(_2\) are shown for the same interval.

![Figure A.1: Daily fluxes for NO\(_x\) for each month of the campaign](image-url)
Calibration check with NO\textsubscript{x}

In Fig. A.3 the calibration check correction test for NO\textsubscript{x} from section 2.1.4 is plotted. Details to the test can be found in this section. Zero air check can be seen at panel A and B while span checks are plotted in panel C and D. Prechamber is switched off on the left side and activated on the right side. Concentrations are given in ppb. pressure in mbar.

**Figure A.3:** The NO\textsubscript{x} concentration is measured for six different pressure levels in the manifold. The manifold pressure is plotted on the x-axis, the concentration for different calibration checks on the y-axis.
**Diurnal NO\textsubscript{x} and compounds-concentration**

In Fig. A.4 the daily concentrations (in ppb) for NO\textsubscript{x} and its compounds are plotted for each month of the campaign. On the left panel the values represent weekday values and on the right panel are weekend values plotted. Tim is given in UTC.

**Figure A.4:** The left panel are the values of the weekday and the right panel are the values of the weekend. The values represent the median on a monthly basis.
Acknowledgments

Such a master thesis would not be possible without people who support one. Therefore, my major thanks belong to my supervisor and mentor Thomas Karl who enabled me to work on such an interesting field. He was a supporter in any matters of the thesis and made it possible to demonstrate my mechanical skills as well. In this context, I would also thank a lot Martin Grauß who showed me how scientists are working on a setup and explained me the mechanical and mathematical background in detail. The thesis is based on a lot of data from different internal and public authorities. Especially Andreas Weber from the government of Tyrol who supported me with traffic load data must be emphasized. Marcus Striednig was supplying flux and quality data for evaluation. Very special thanks are for the employees of the scientific working group “Atmospheric Physics and Chemistry” conducted by Univ.-Prof. DI Dr. Thomas Karl who became friends. Although there was stressful time already my girlfriend was supporting me all the time and helped me to relax as well. The most wonderful moment in my life happened also during writing my master thesis and therefore a special thanks to the “Universe” for my son Florian Otto who gave me a lot of strength. But that all would not be possible without my family who supported me since my birth. Whether financially or mentally my family gave me the feeling to do the right. – Thank you!
Curriculum Vitae

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2012 – 2017 Master study at the University of Innsbruck. Master of Natural Science in Atmospheric Science.

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FURTHER SKILLS:

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Languages       German, English
Eidesstattliche Erklärung

Ich erkläre hiermit an Eides statt durch meine eigenhändige Unterschrift, dass ich die vorliegende Arbeit selbständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe. Alle Stellen, die wörtlich oder inhaltlich den angegebenen Quellen entnommen wurden, sind als solche kenntlich gemacht.

Die vorliegende Arbeit wurde bisher in gleicher oder ähnlicher Form noch nicht als Magister-/Master-/Diplomarbeit/Dissertation eingereicht.

________________________  ______________________
Datum                              Unterschrift