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Investigating the Personal Exposure of NO_2 for Cyclists – A Field Test in Heidelberg

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Abstract

Nitrogen dioxide (NO_2) is an air pollutant in urban areas that attracted great public attention over the past years. In this thesis we analysed the exposure of cyclists to NO_2 in Heidelberg using an ICAD measurement system. Along a 20km route through Heidelberg, measurement runs were executed in winter, spring and summer time; during rush hours in the morning and evening as well as during off-peak times on various weekdays. The mean NO_2 concentration we measured along the route was $40\mu g/m^3$and therefore just as high as the official guideline thresholds for the annual mean value. In addition, we executed point measurements at four different locations (in total 19 hours of measurements at different times of the day). The hourly mean concentrations at these locations, highly frequented by cyclists, pedestrians but also motorized vehicles, showed strong fluctuations in the range of $9\mu g/m^3$ to $74\mu g/m^3$. In order to allow predictions about the annual mean NO_2 concentrations based on our measurements, we analysed the diurnal and seasonal variations of the hourly means of NO_2, measured by the governmental measurement station at Berliner Straße in Heidelberg. With the help of these results we extrapolated our measurement data to annual mean and rush hour concentrations. For the mean concentrations that we extrapolated for rush hours, we found that for large streets the concentrations varied between $42\mu g/m^3$ and $96\mu g/m^3$.

Stickstoffdioxid (NO_2) ist ein Luftschadstoff, der vor allem in städtischen Gebieten problematische Konzentrationen erreicht und in den vergangenen Jahren für politische Diskussion gesorgt hat. In dieser Bachelorarbeit haben wir unter Verwendung eines ICAD Messinstrumentes die Belastung durch NO_2 von Fahrradfahrern in Heidelberg untersucht. Entlang einer 20km langen Route durch Heidelberg wurden Messungen unter winterlichen und frühlinghaften bzw. sommerlichen Bedingungen ausgeführt. Dabei fanden die Messungen sowohl zur Hauptverkehrszeit als auch zu Zeiten mir wenig Verkehr statt. Die mittlere NO_2 Konzentration all unserer Messungen betrug $40\mu g/m^3$; dies entspricht gerade dem gesetzlich erlaubten Jahresdurchschnitt. Weiterhin wurden an vier Standorten jeweils einstündige Punktmessungen mehrfach durchgeführt. Insgesamt wurden dadurch Standdaten in einem Umfang von 19 Stunden Gesamtmesszeit zu verschieden Tageszeiten gewonnen. Die Stundenmittelwerte an den stark von Fußgängern und Radfahrern frequentierten Messpunkten variierten stark zwischen $9\mu g/m^3$ und $74\mu g/m^3$. Um auf Grundlage unserer Messdaten Aussagen über die jährliche Durchschnittsbelastung treffen zu können, analysierten wir die tageszeitlichen und saisonalen Schwankungen der NO_2 Belastung an der durch die Landesanstalt für Umwelt Baden-Württemberg (LUBW) betriebenen Messstation an der Berliner Straße. Unter Zuhilfenahme dieser Ergebnisse extrapolierten wir unsere Messdaten zu jährlichen Durchschnittskonzentrationen, sowie zu für Hauptverkehrszeiten üblichen Durchschnittswerten. Die extrapolierten Durchschnittskonzentrationen zur Hauptverkehrszeit lagen bei großen Straßen zwischen $42\mu g/m^3$ und $96\mu g/m^3$.

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1. Introduction

NO_x is a summary term for the two nitrogen oxides NO (nitric oxide) and NO_2 (nitrogen dioxide). Today NO_x gases are considered to be among the most problematic pollutants in urban areas not only in developing but also in industrialized countries. It is not only that they are harmful gases themselves. Their occurrence also influences the production of O_3 (ozone) and the abundance of OH (hydroxyl radicals) in the air. Therefore NO_x also play an important role for the so called "Los Angeles Smog", a phenomenon describing exceptionally high concentrations of ozone in urban areas during summer. [1, p. 9] There are various sources for the production of NO_x. In nature, NO_x can for example be emitted by the soil or lightning during thunderstorms. However, in urban areas the main sources for NO_x are anthropogenic. NO_x are formed in combustion processes at high temperatures. Therefore, motorised vehicles, heating systems based on oil, coal, wood or gas as well as industries lead to manmade emissions of NO_x. [2] In Table 1 we can find an overview of the most important sources for NO_x. As we can see, half of the approximated NO_x emissions are caused by industry and traffic.

Table 1 Main anthropogenic and natural sources for global tropospheric NO_x, taken from [3, p. 9]

NO_x-Sources	Emission (10^{12} g/a)	Uncertainty (10^{12} g/a)
Industry and Traffic	22.00	13.00-31.00
Biomass Burning	7.90	3.00-15.00
Soil Emission	7.00	4.00-12.00
Thunderstorm	5.00	2.00-20.00
Air Traffic	0.80	0.59-0.95
Stratospheric Production	0.64	0.40-1.00
Total	44.00	23.00-8.00

In urban areas the traffic and industry play an even more important role. In the case of Heidelberg, the city where all of the measurements for this thesis were done, we find that in 2000, more than 85% of the anthropogenic NO_x emissions were caused by traffic (see Figure 1; unfortunately there was no more recent data available for Heidelberg, and more recent data for Germany is not suitable, as Heidelberg has industrial facilities emitting NO_2 below the German average). For this reason we can expect that the people who are exposed to the highest concentrations of NO_X in Heidelberg are people in the traffic like car passengers and cyclists, as they are close to the sources of NO_x. Note that

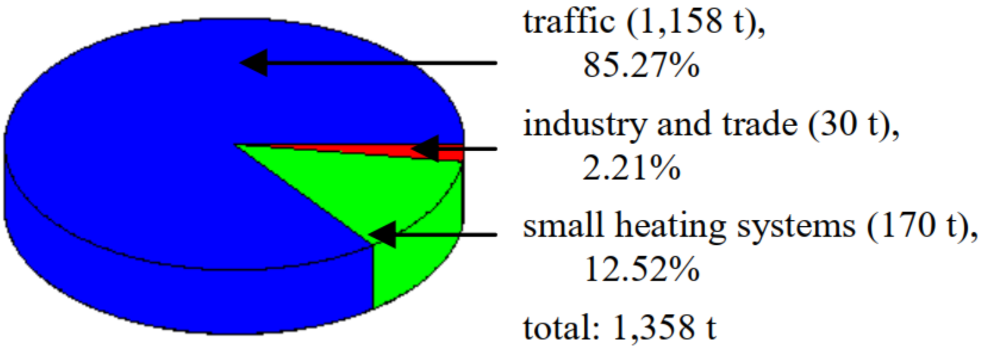

Figure 1 Anthropogenic emissions of NO_x in the year 2000 just for the city of Heidelberg from [3, p. 11](unfortunately there was no more recent data available)

Since NO_x is an irritant gas, it harms the mucous membrane in the whole respiratory tract and irritates the eyes. Furthermore, short time exposure is related to effects on the pulmonary function, an increase in hospital admissions and an increase in mortality. Long-time exposure, on the other hand, is related to a reduction in the lung function and an increased probability of respiratory symptoms. However, we need to keep in mind that the abundance of NO_x also influences other pollutants such as ozone and inorganic particle matter (PM). Therefore, the health impacts of these secondary pollutants also need to be considered when assessing the impact of NO_x. [1] [2]

To protect their inhabitants from these health hazards, the European Union has introduced two different threshold values for NO_2 in the EU-Directive 2008/50/EC. First, the annual mean concentration that a person is exposed to must not exceed $40\mu g/m^3$. Second, an hourly mean of $200\mu g/m^3$ must not be exceeded more than 18 times per year. [2] These threshold values did agree with the official guidelines of the World Health Organisation from 2005. [4, p. 16] However, since then the WHO has lowered the recommended guidelines for the annual mean to $20\mu g/m^3$. [5] At the moment about 500 measurement stations survey the NO_2 pollution in Germany. Among those which are situated relatively close to the traffic, 44% registered an annual mean concentration exceeding the threshold of $40\mu g/m^3$. [2] In absolute numbers this corresponds to 65 cities. The highest annual mean values in 2017 were measured in Munich and Stuttgart, reaching even $78\mu g/m^3$ and $73\mu g/m^3$ respectively. [6]

2. Theory

2.1. Nitrogen Oxides

As mentioned before, the largest source of NO_x in urban areas is anthropogenic. However, NO_x is usually created in the form of NO. Under conditions of high temperatures followed by a fast cooling (as for example in combustion processes), the triple bonds of N_2 are dissociated and NO can be formed. This is described by the Zel'dovic cycle in (1) from [1]. M corresponds to a reaction partner that ensures the conservation of momentum.

$$
\begin{aligned}
O_2 + M &\longrightarrow O + O + M \\
O + N_2 &\longrightarrow NO + N \\
N + O_2 &\longrightarrow NO + O \\
N + OH &\longrightarrow NO + H
\end{aligned}
\tag{1}
$$

Afterwards, several processes can convert NO into NO_2, the trace gas that we detected with our measurement instrument.

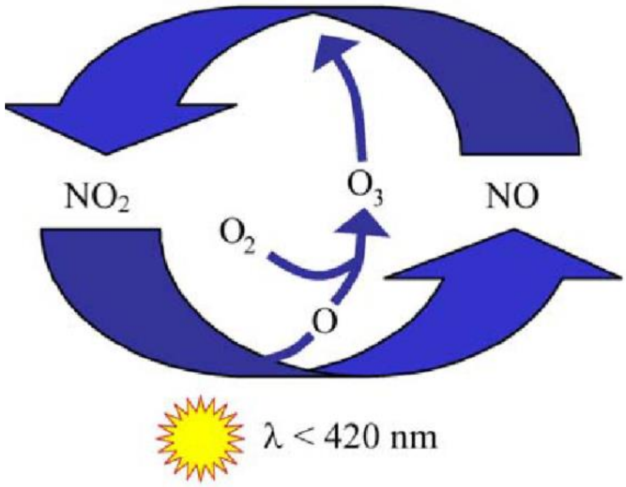

Figure 2 Photo-stationary state between NO, NO_2 and O_3 under the absence of organic compounds, from [3].

Under the presence of ozone (O_3) NO_2 can be formed

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (2)$$

However, during daytime the part of the solar radiation that has a wavelength $\lambda < 420nm$ NO_2 can photo dissociate NO_2 back to NO, creating atomic oxygen that can form O_3 again.

$$\begin{aligned} NO_2 + h\nu_{\lambda<420nm} &\longrightarrow NO + O(^3P) \\ O(^3P) + O_2 &\xrightarrow{M} O_3 \; with \; M = O_2, N_2, \ldots \end{aligned} \qquad (3)$$

This leads to the photo-stationary state between NO, NO_2 and O_3. The cycle is presented in Figure 2. At typical O_3 mixing ratios of 30ppb the [NO]/[NO_2] ratio near the ground is close to one. [3, p. 13]

In the presence of volatile organic compounds (VOCs), the situation changes, as another reaction to form NO_2 out of NO is possible without the destruction of O_3. With the help of OH radicals hydro carbons RH can form the peroxy radical RO_2

$$\begin{aligned} RH + OH &\longrightarrow R + H_2O \\ R + O_2 &\longrightarrow RO_2 \end{aligned} \qquad (4)$$

This peroxy radical can then convert NO into NO_2 while forming RO. In the next step RO can form another peroxy radical, HO_2. HO_2 will then help to form another NO_2 molecule.

$$\begin{aligned} RO_2 + NO &\longrightarrow RO + NO_2 \\ RO + O_2 &\longrightarrow R'CHO + HO_2 \\ HO_2 + NO &\longrightarrow NO_2 + OH \end{aligned} \qquad (5)$$

Together with the photo-dissociation in (3) this leads to the effective equation for the ozone production:

$$\mathrm{RH} + 4\,\mathrm{O_2} + 2\mathrm{h\nu}_{\lambda<410\,\mathrm{nm}} \longrightarrow \mathrm{R'CHO} + \mathrm{H_2O} + 2\,\mathrm{O_3} \qquad (6)$$

The water soluble compounds HNO_3 (nitric acid) and HONO (nitrous acid) are the most important sinks of nitrogen oxides once they are absorbed by aerosols or water droplets. [3, p. 13] Once the aerosols deposit on the ground or the water droplets (e.g. rain) drain away in the soil, the nitrogen oxides are removed from the air. The corresponding chemical reaction to form HNO_3 relies on the presence of OH:

$$NO_2 + OH \xrightarrow{M} HNO_3 \tag{7}$$

Alternatively HNO_3 can be formed with the help of O_3 in the absence of sunlight [7, p. 8], [1]

$$\begin{aligned} NO_2 + O_3 &\longrightarrow NO_3 + O_2 \\ NO_3 + NO_2 &\xrightarrow{M} N_2O_5 \\ N_2O_5 + H_2O &\longrightarrow 2HNO_3 \end{aligned} \tag{8}$$

2.2. Lambert-Beer Law

The main part of our measurement system is a combination of an LED, an optical resonator with highly reflective mirrors and a spectrometer. To determine the concentration of NO_2 in the sample air in the optical resonator, we use the Lambert-Beer-Law:

$$I(\lambda, L) = I_0(\lambda)\exp(-\epsilon(\lambda)L) \tag{9}$$

It states that the Intensity I_0 of light with a wavelength λ, transmitted through a material with absorption coefficient ϵ for a distance L, has decreased exponentially to the intensity I. The absorption coefficient ϵ consists of the concentration of the absorber c and the absorption cross-section σ:

$$\epsilon(\lambda) = c\,\sigma(\lambda) \tag{10}$$

For the following it will be useful to define the optical density D

$$D(L, \lambda) := \ln\left(\frac{I_0(\lambda)}{I(\lambda, L)}\right) = c\sigma(\lambda)L \tag{11}$$

To apply this relationship in our measurements, we need to consider that the trace gas concentration might vary at different parts of the light path. Also, we usually have more than only one absorber. With the average concentration $\bar{c}_j$ of the absorber j along the light path this leads to

$$D(L, \lambda) = L \cdot \sum_{j=1}^{n} \bar{c}_j \sigma_j(\lambda) \tag{12}$$

In order to calculate the average concentration along the light path of a single absorber $\bar{c}$ we then write:

$$\bar{c} = \frac{D(\lambda)}{\sigma(\lambda)L} \tag{13}$$

2.3. Differential Optical Absorption Spectroscopy (DOAS)

In practice we will need to apply some further tricks and consider some additional effects to successfully determine the NO_2 concentration. The absorption coefficient ϵ can be separated into three different parts that influence the decrease of intensity of a light beam. Apart from the absorption of the light by trace gases S, Rayleigh scattering and Mie scattering play a role. This gives us

$$\epsilon\,(\lambda) = \epsilon_S + \epsilon_{Ray} + \epsilon_{Mie} \tag{14}$$

Rayleigh scattering describes the scattering on air molecules that are smaller than the wavelength of the light while Mie scattering describes the scattering on aerosols, which are larger than the wavelength. In addition, the cross-section $\sigma(\lambda)$ can be split into a narrowband component σ^n and a broadband component σ^b:

$$\sigma(\lambda) = \sigma^n(\lambda) + \sigma^b(\lambda) \tag{15}$$

Substituting (14) and (15) in (9) we get:

$$I(\lambda, L) = I_0 \exp\left(\sum_{j=1}^{n} L\left(\sigma^b(\lambda) + \sigma^n(\lambda)\right) c_j + L\left(\epsilon_{Ray}(\lambda) + \epsilon_{Mie}(\lambda)\right) \right) \tag{16}$$

We can simplify this equation if we define a new $I_0'(\lambda)$ that includes the broad band absorption as well as the Rayleigh and Mie scattering.

$$I(\lambda, L) = I_0'(\lambda) \exp\left(\sum_{j=1}^{n} L\sigma^n(\lambda) c_j \right) \tag{17}$$

Using $I_0'(\lambda)$ we can then define a new optical density, the differential optical density:

$$D'(\lambda, L) = \ln\left(\frac{I_0'(\lambda)}{I(\lambda, L)}\right) = \sum_{j=1}^{n} L\sigma^n(\lambda) c_j \tag{18}$$

With the help of (18) it is possible to determine the concentration of all the trace gases as for example O_3, BrO or NO_2. We can even measure them at the same time because each trace gas has its own characteristic fingerprint in the differential absorption spectrum as can be seen at the selected trace gases in Figure 3.

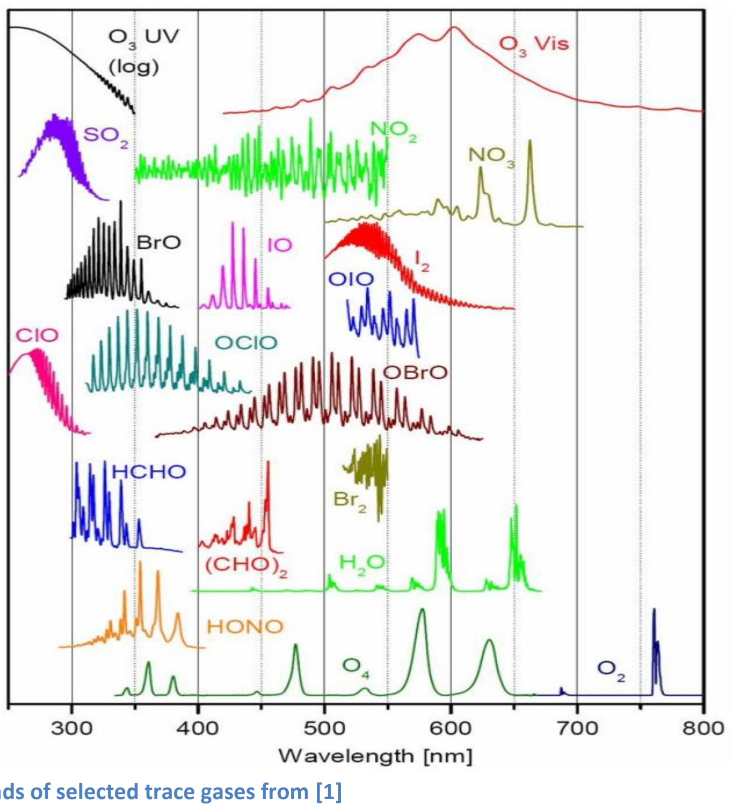

Figure 3 Absorption bands of selected trace gases from [1]

In order to determine the trace gas concentrations it is possible to perform a DOAS fit. Based on (18), it varies the fit parameters a_i and b_k to minimize the quadratic deviation of

$$\min\left[\sum_{i=1}^{n}\sigma_i^n(\lambda)a_i+\sum_{k=1}^{m}b_k\lambda^k-\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right)\right]^2 \tag{19}$$

The polynomial is to model the broad band absorption while $I(\lambda)$ and $I_0(\lambda)$ are the measured intensities. The coefficients a_i are a measure of trace gas concentration:

$$c_i=\frac{a_i}{L} \tag{20}$$

Our problem now is twofold: On the one hand, the concentration c_i is usually very small for trace gases. This means L must be big enough in order to detect the light absorption caused by the trace gas. On the other hand, we need to know L as precisely as possible to keep the measurement error small. To implement a large light path in the small instrument box, we use an optical resonator with two highly reflective mirrors as can be seen in Figure 4. The light enters the optical resonator on one side, and each time it reaches a mirror, only a very small part of the light is transmitted. This way, the light that reaches the optical fibre behind the mirror on the opposite side has, on average, travelled a distance of more than one kilometre.

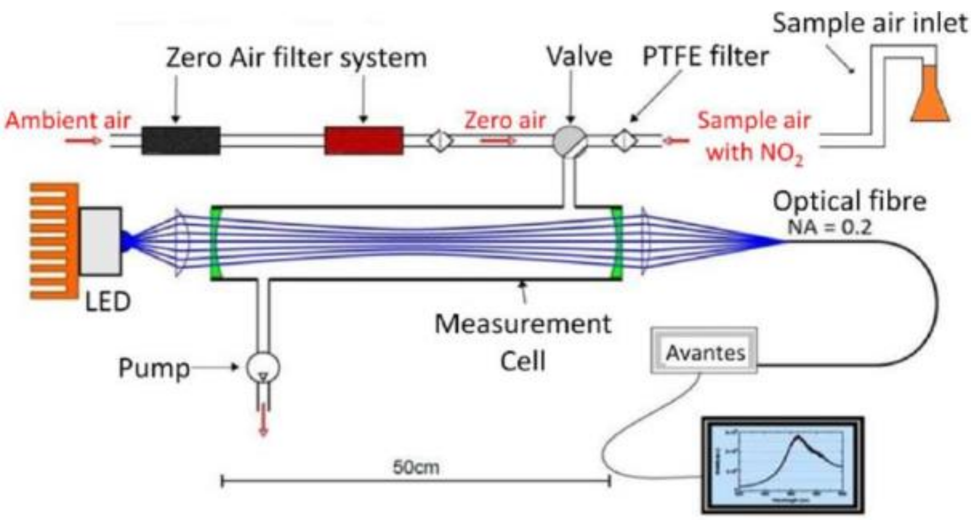

Figure 4 Setup of the ICAD-instrument used for our measurements from [7].

The total intensity I_{out} of the light that has passed the optical resonator is composed as follows:

$$\begin{aligned} I_{out} &= I_{in}T_{M,1}T_{gas}T_{M,2} && (one\ reflection) \\ &+I_{in}T_{M,1}T_{gas}R_2T_{gas}R_1T_{gas}T_{M,2} && (two\ reflections) \\ &+\cdots \\ &+I_{in}T_{M,1}T_{gas}R_1^nR_2^nT_{gas}^{2n}T_{M,2} && (2n\ reflections) \\ &+\cdots \\ &= I_{in}T_{M,1}T_{gas}T_{M,2}\sum_{n=0}^{\infty}R_1^nR_2^nT_{gas}^{2n} \end{aligned} \tag{21}$$

Here we introduced the transmission coefficients T_M and the reflection coefficients R_M and R_{gas} of the mirrors and the gas respectively. The different light paths of the light beams described by (21) are sketched in Figure 5.

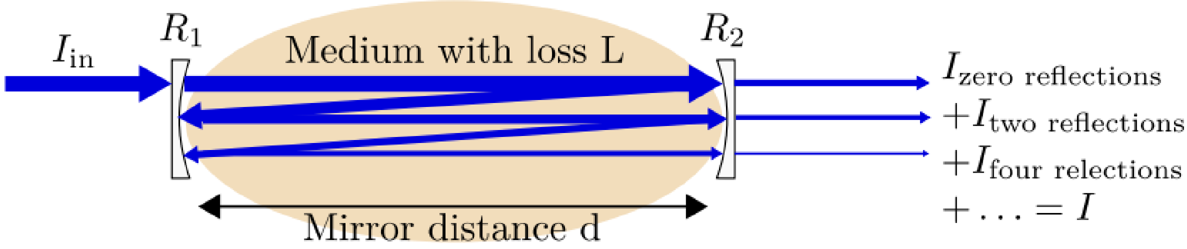

Figure 5 Sketch of the light paths through a CE-DOAS cavity from [1]

To avoid dependencies on the Intensity of the light source and the transmissivity of the mirrors, we will consider the cavity enhanced optical density:

$$D_{CE}(\lambda) = \ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right) \tag{22}$$

Note that from now on $I_0(\lambda)$ and $I(\lambda)$ do no longer describe the intensity at the beginning and at the end of the light path. By now, $I_0(\lambda)$ and $I(\lambda)$ describe the intensity transmitted when the optical resonator is flooded with zero air (filtered air that contains no light absorbing trace gases or aerosols) and the intensity transmitted when the optical resonator is filled with sample air (containing additional absorbers) respectively. Of course, zero air still has an absorption coefficient that cannot be neglected. We therefore define the difference of the absorption coefficients from the sample air and zero air as

$$\epsilon_\Delta \coloneqq \epsilon - \epsilon_0 = \sum_{i=1}^{n} \sigma_i \bar{c}_i \tag{23}$$

With the assumptions that $\epsilon \to 0$ *and* $R \to 1$ it can be shown that

$$D_{CE}(\lambda) = \ln\left(1 + \frac{d\epsilon_\Delta(\lambda)}{1 - R(\lambda) + d\epsilon_0(\lambda)}\right) \tag{24}$$

And therefore

$$\frac{I_0(\lambda)}{I(\lambda)} - 1 = \frac{d\epsilon_\Delta(\lambda)}{1 - R(\lambda) + d\epsilon_0(\lambda)} \tag{25}$$

Keeping this in mind we define the effective light path, the path the light would travel to be absorbed to the same extend as in the optical resonator:

$$\begin{aligned} \bar{L}_{eff}(\lambda) &\coloneqq \frac{D_{CE}(\lambda)}{\epsilon_\Delta} \\ &= \frac{D_{CE}(\lambda)}{\exp(D_{CE}(\lambda)) - 1} \frac{d}{1 - R(\lambda) + d\epsilon_0(\lambda)} \\ &= \frac{D_{CE}(\lambda)}{\exp(D_{CE}(\lambda)) - 1} \bar{L}_0(\lambda) \end{aligned} \tag{26}$$

In the second step we have replaced ϵ_Δ using (25), and in the last step we introduced $\bar{L}_0$ as the effective light path for $\lim_{D_{CE}\to 0}(\bar{L}_{eff})$ in the limiting case of no absorbents in the optical resonator.

The first factor in the last line describes the path length reduction due to the presence of absorbers. In the last step we need to determine $\bar{L}_0$. As helium shows only very weak Rayleigh scattering (about 100 times weaker than zero air), it causes a strong intensity change at the output of the optical resonator compared to zero air. Using (24) and measuring the intensities for an optical resonator flooded with zero air and helium respectively we can now determine $\bar{L}_0$.

We can now fit our trace gas concentrations with the CE-DOAS method using

$$D_{Fit}(\lambda) = \sum_{i=1}^{n} r_i(\lambda)\bar{c_i} + \sum_{k=1}^{m} b_k \lambda^k \tag{27}$$

The wavelength depended coefficients $r_i(\lambda)$ are defined as

$$r_i(\lambda) = \bar{L}_{eff}(\lambda)\sigma_i(\lambda) \tag{28}$$

The problem with this fit is one assumption that was made here. I_{in} needs to be the same intensity in (21) for the measurement of I and I_0. This is not always true because of thermal or mechanical influences. To cope with this, the Iterative Cavity DOAS (ICAD) algorithm is used as is described in further detail in the dissertation of Dr. Martin Horbanski. [8] First $L_0(\lambda)$ is used in (19) and (20) to determine a first approximation of the trace gas concentrations. These approximated concentrations can then be used for the determination of $\bar{L}_{eff}$ which in turn can be used to determine new fit parameters. This iterative process lasts until either a certain number of iterations have been reached or the quadratic deviation becomes lower than a given threshold.

3. Measurements

3.1. Measurement System

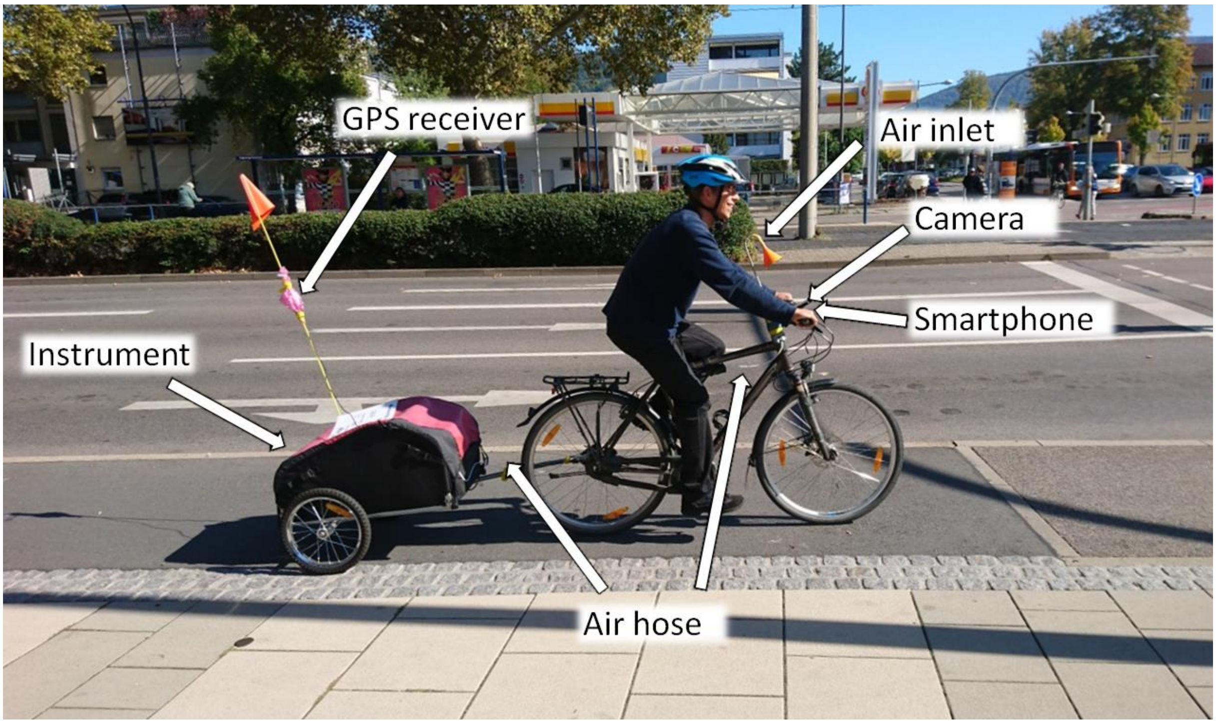

Figure 6 Measurement set-up

All of our NO_2 measurements were executed using an ICAD measurement system, carried in a bike trailer. Additionally, a battery for electricity supply, an air filter, a GPS receiver, a camera and a smartphone were fixed on the bike. The whole set-up can be seen in Figure 6.

The ICAD itself was in a box embedded in foamed material to protect it against vibrations and shocks during the bike rides. As the temperature of the surroundings fluctuates a lot for outdoor measurements, the box was held at a constant temperature of 32°C by a Temperature Stabilisation Electronic (TSE 1.1)) with Peltier element to guarantee a stabile optic and avoid water condensation. The GPS receiver was fixed at the flag of the trailer to ensure the best reception possible. To be able to find the cause for exceptional NO_2 concentrations during the evaluation, a camera (GoPro Hero3+) was fixed to the handlebar, taking pictures every five seconds. This way one could analyse, whether, for example, a bus in front of the bike had caused an exceptional peak in NO_2 concentrations. The smartphone was fixed to the handlebar and received live data of the measurement system via a WLAN connection. This way the cyclist could survey the measurement system and immediately see the measured NO_2 concentration as well as his GPS position. For the electricity supply a mobile LiPo battery was stored in the bike trailer. The zero air filter system, also stored in the trailer, was used to flush the measurement system with clean air at the end of a measurement trip. For the inlet of sample air we installed a hose (PTFE) from the trailer to the handlebar, ending in a funnel to protect it against rain and other solids or liquids that are not supposed to be sucked up into the measurement instrument by the air pump. The weather data used in the evaluation for all measurements was taken from the weather station of the Institute for Environmental Physics (IUP), Heidelberg.

3.2. Route Measurement

3.2.1. Description of the Route

Figure 7a Mittermaier Straße (number 12 in Figure 8), main road with high traffic volume

Figure 7b Neuenheimer Landstraße (number 10 in Figure 8), side road with medium traffic volume

Figure 7c Gaisbergstraße (number 22 in Figure 8), side road with low traffic volume

Figure 7d Field path (number 2 in Figure 8), path with no traffic

Figure 7 Overview over different street types of our measurement route

The measurement route that was used for data collection can be seen in Figure 8. As it was the purpose of this Bachelor thesis to continue the measurements executed by Richard Brenner in

November and December 2017, the route is almost the same as for his measurements. The route chosen for the measurement trips was 20 km long and contained streets of different categories frequently used by cyclists as can be seen in Figure 7. The categories are:

- Existence of a bike path and distance to motorized traffic
- Traffic volume
- Urban canyon or free air exchange due to building density and height
- Number of lanes
- Speed limit

On the basis of these categories we divided the route in 27 sections represented in Figure 8 and Table 2. The ranking for the different categories of the various streets in Table 2 is based on our own assessment as well as data from OpenStreetMap (OSM) if available.

Two stations for permanent air quality measurements, run by the "Landesanstalt für Umwelt Baden-Württemberg" (LUBW), were passed on each tour, allowing a better comparability of our measurements to the measuring stations that permanently check the NO_2 concentration in air. The "Landesanstalt für Umwelt Baden-Württemberg" (LUBW) is an environmental agency, run by the state. The measurement station situated at Mittermaierstraße ("Station B" in Figure 8) only measures annual mean values with a passive sampler while the measurement station at Berliner Straße ("Station A" in Figure 8) also measures hourly mean values that we can access and use for our evaluation. In the following we will therefore always refer to the measurement station at Berliner Straße, if not explicitly specified.

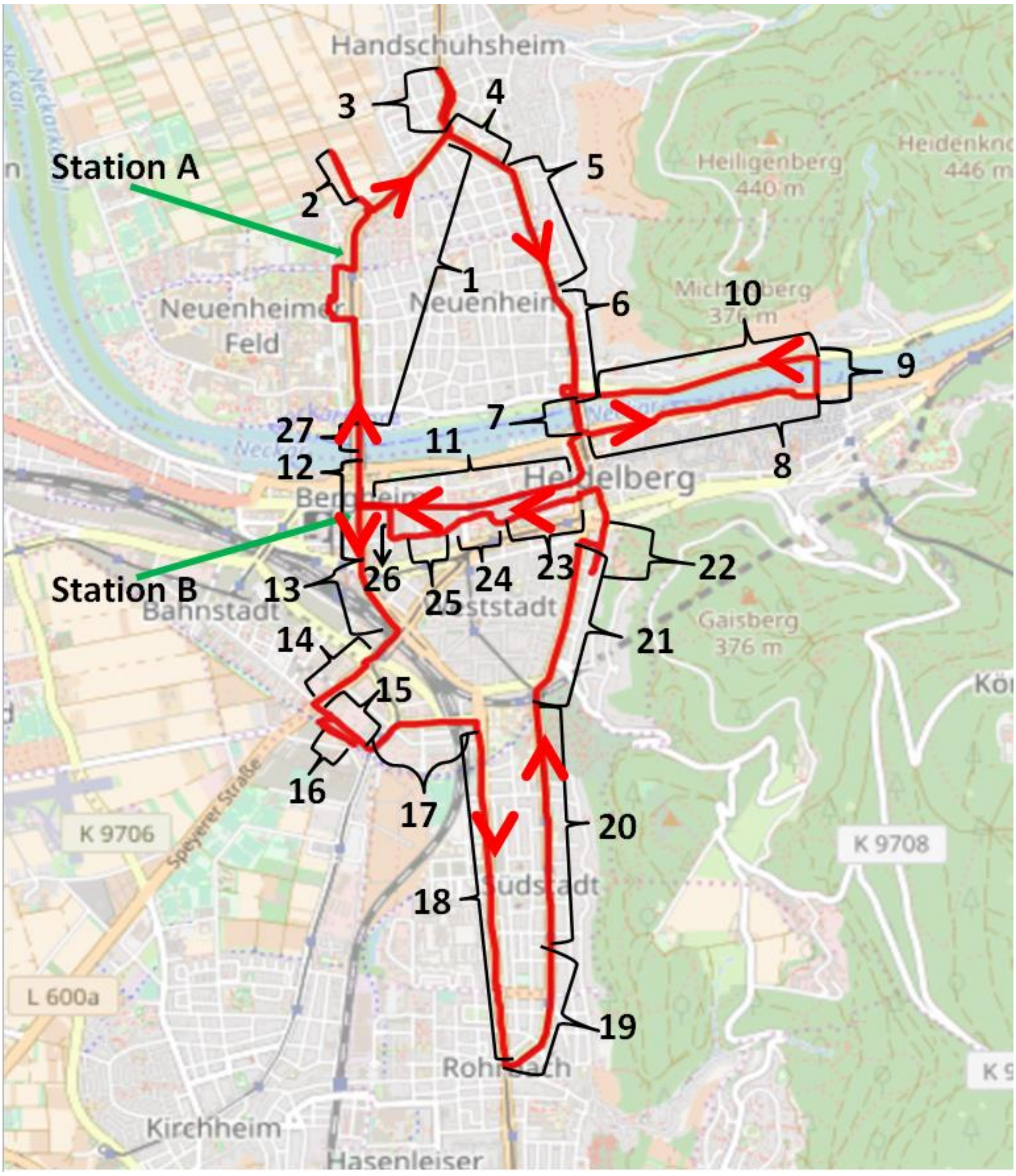

Figure 8 The measurement route with all the different streets, described in Table 2. Station A is the measurement station at Berliner Straße from LUBW with 1h NO_2 data; station B is the spot measurement station at Mittermaierstraße from LUBW with annual mean passive sampler measurements.

Table 2 Properties of all streets that are part of the route. The column "urban canyon" evaluates the distance and height of buildings or big trees that encumber air exchange. Data in the columns marked with "(OSM)" is taken from OpenStreetMap [7]. Even though OpenStreetMap often gives the number of lanes only for one direction we counted both directions for a higher informative value.

Number	Street	Bike path categories [1] (own rating)	Cycleway category (OSM)	Traffic volume (own rating)	Urban canyon (according to character of surrounding, own rating)	Number of marked lanes on street (all directions)	Number of lanes (OSM, most times only one direction)	Street type (own rating)	Street type (OSM)	Speed limit (OSM)
1	Berliner Straße	2	-	High	No	4	2	Main	Primary	50
2	Field path	3	-	None	No	1	1	Side	Track	-
3	Dossenheimer Landstraße	3	-	High	By trend	2	2	Main	Primary	50
4	Rottmannstraße	2	Lane	Medium	Yes	2	2	Main	Primary	50
5	Steubenstraße	2	Lane	Medium	North part due to big trees	2	2	Main	Primary	50
6	Brückenstraße	2	Lane	Medium	Yes	2	2	Main	primary	30
7	Theodor Heuss bridge	2	Use_sidepath	Medium	No	4	2	Main	Primary	50
8	Neckarstaden	2	-	High	No	2	2	Main	Primary	50
9	Alte Brücke (old bridge)	3	-	None	No	1	1	Side	Living street	-
10	Neuenheimer Landstraße	2	-	Medium	No	2	2	Side	Secondary	30
11	Bergheimer Straße	3	-	Medium	Yes	2	1	Side	Tertiary	30
12	Mittermaierstraße	2	-	High	Yes	4	1	Main	Primary	50

[1] Categories for the bike path: 1: bike path several tens of meters away from the car lane, 2: bike path next to car lane, 3: no bike path separated from the car lane

13	Lessingstraße	2	-	High	No	4	2	Main	Primary	50
14	Speyerer Straße	2	No	High	No	4	2	Main	Primary	50
15	Rudolf-Diesel-Straße	3	-	Low	No	2	2	Side	Residential	50
16	Bike path along old tracks	1	Designated	None	No	1	-	Side	Path	-
17	Hebelstraße	3	Yes	Medium	No	2	2/1	Side	Secondary/tertiary	50
18	Römerstraße	2	-	High	No	4	2	Main	Primary	50
19	Karlsruher Straße	2/3	-	Low	Yes	2	-	Side	Secondary	20/50
20	Rohrbacher Straße (south)	2	Lane	Medium	No	2	-	Side	Primary	50
21	Rohrbacher Straße (north)	3	Lane	High	Yes	2	-	Main	Primary	50
22	Gaisbergstraße	3	-	Low	Yes	1	1	Side	Residential	30
23	Poststraße	3	-	Low	No	1	-	Side	Residential	30
24	Alte Bergheimer Straße	3	-	Low	Yes	1	-	Side	Residential	30
25	Alte Eppelheimer Straße	3	-	Low	No	1	-	Side	Residential	30
26	Kirchstraße	3	-	Low	Yes	1	-	Side	Residential	30
27	Ernst Walz bridge	2	-	High	No	4	2	Main	Primary	50

3.2.2. Executed Measurements on the Route

In total, the whole route was measured 24 times. Thereof, 4 complete runs were executed under winter conditions with low temperatures and sometimes snow (see bachelor thesis of Richard Brenner [7]). The other 20 complete runs were performed from April to July under summer conditions with moderate to high temperatures. Additional to the 24 runs, another 11 runs on parts of the route were executed throughout the year. An overview over all measurements along the route is given in Table 13 in the appendix. As not all tours covered the whole route (shown in Figure 8), the column "description of route" describes the route, giving the numbers of the measured streets. The streets that belong to the numbers can be found in Table 2 or in Figure 8. Additional point measurements interrupted some bicycle measurements on the route (indicated by a comma in Table 13). A single measurement run of the whole route takes about two hours. In this time the urban background NO_2 concentration changes. This is the reason for the extrapolation of the data as described in chapter 4.

3.3. Point Measurements

3.3.1. Description of the Point Measurement Site

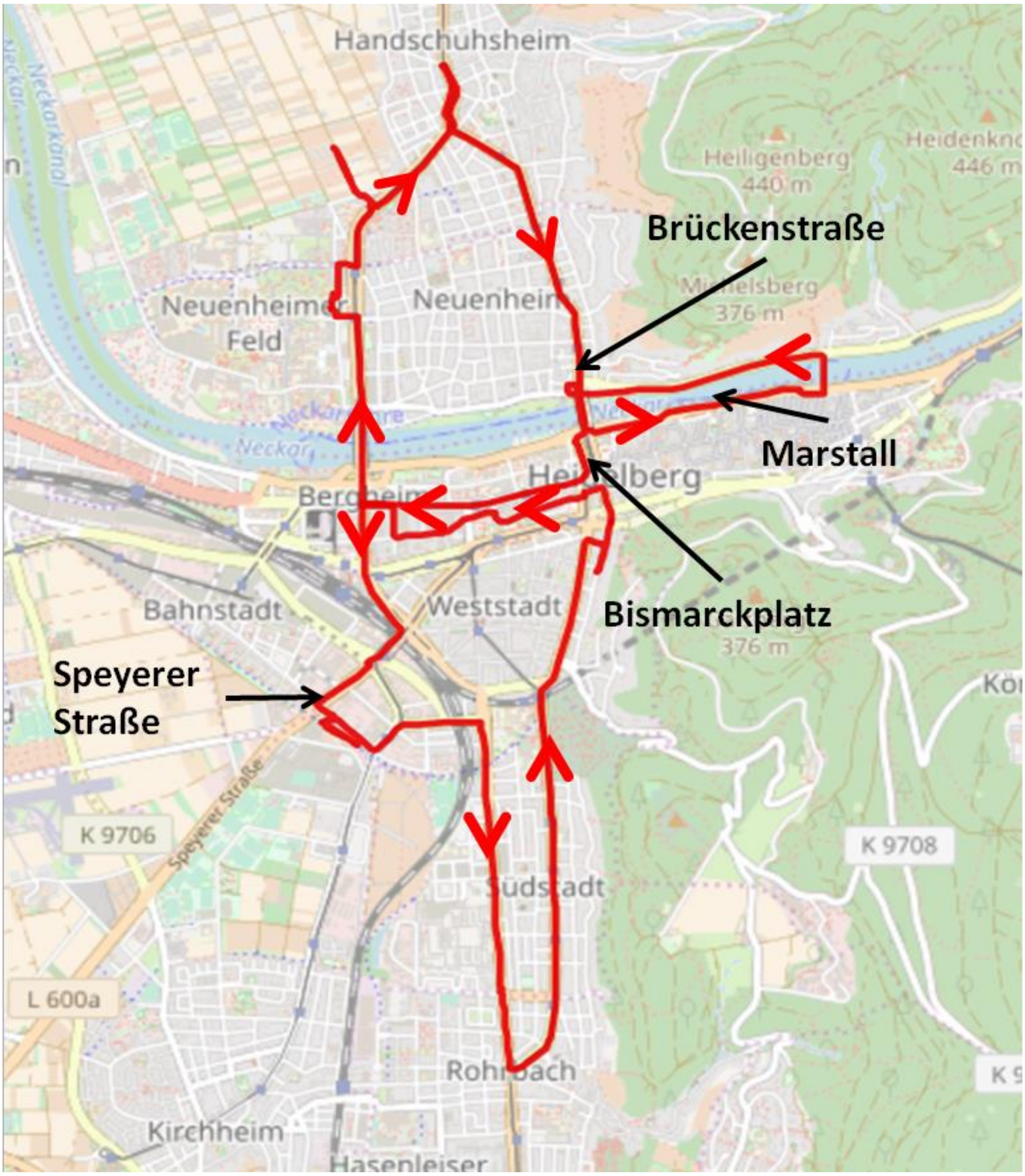

Figure 9 Location of all four point measurement sites

In addition to the measurement tours we also executed single point measurements at four locations in Heidelberg marked in Figure 9 (a map section for each site can be found in Figure 29, Figure 30, Figure 31 and Figure 32 in the appendix). All places are frequented by many pedestrians and cyclists. In Figure 10a-d photos of the locations can be found. The exact places where the measurement instrument was placed is marked in the photo. For all point measurements the funnel with the sample air inlet was taken from the bike handle bar and fixed in a height of 1.8 meters above the ground.

Figure 10a Measurement point at Brückenstraße

Figure 10b Measurement point at Bismarckplatz

Figure 10c Measurement point at Neckarstaden close to Marstall

Figure 10d Measurement point at Speyerer Straße

Figure 10 Measurement sites for point measurements. The symbol indicates the position of our measurement instrument.

3.3.1.1 Brückenstraße

The first measurement site was located at Brückenstraße close to the bridge across the Neckar. At the measurement point the buildings are high on either side forming a street canyon accumulating NO_2 and other pollutants in the air. Due to many cars, trucks and busses that pass this point at every time of the day, we expected to measure relatively high concentrations of NO_2 there. Additionally, many pedestrians and cyclists pass this point, and are therefore affected by the polluted air. The distance of our sample air point to the traffic lane of motorized vehicles was about 3 meters; the bike path was in between.

3.3.1.2 Bismarckplatz

The next measurement point was located at the west part of the Bismarckplatz, a square that is usually crowded with people meeting up or waiting for the next tram to come when returning from a walk in the main street in Heidelberg. On the one hand, the air all over the square should be well circulated and therefore low in pollutants; on the other hand, the traffic around the square is dense. There are lots of busses stopping at the Bismarckplatz and at the same time emitting lots of NO_x. Additionally, there are a couple of traffic lights around the square, meaning that many vehicles are accelerating regularly. Due to the huge number of affected pedestrians, we included this place to our set of point measurements. The distance to the next road, frequented by cars, was about 6 meters, the same as the distance to the bus stop.

3.3.1.3 Neckarstaden/B37

Of special interest was also the measurement point at Neckarstaden/B37 located at the bus station Marstallstraße close to the Marstall. Here we have a road well frequented by cars but also trucks and some buses. However, at the same time, the river Neckar delimitates the road on one side. Only a footpath and some huge plane trees are in between the riverbank and the road. Now the exciting question is: To which extend can the free air circulation over the water surface lower the pollution on the street? And how much do the trees insulate the road against the air exchange? As we expect strong variations of the NO_2 concentration around this area, it is important to mention that the measurement point was 5 meters away from the traffic lanes on the side of the road opposite the river.

3.3.1.4 Speyerer Straße

Last but not least, we choose a measurement point at Speyerer Straße in the south of Heidelberg. The point is just next to a distributor road from the motorway in the southwest of Heidelberg. Many commuters use this road every day to drive to their workplace in the city of Heidelberg. Usually the traffic flow is steadier than at Bismarckplatz but in Speyerer Straße we can find several traffic lights as well. On the side of the street we measured, the cars pass a traffic light 50 meters before passing the air sampler. Some of the new buildings nearby are quite high, but just around our selected point the footpath itself is 10 meters wide and a carpark as well as a grass strip allow the air to circulate. The distance from our measurement point to the side of the traffic lane was 2 meters. In between the cyclists could pass on the bike path.

3.3.2. Executed Measurements at the Point Measurement Site

At the four different locations, as described above, we measured the NO_2 concentration for about one hour each at different times of the day. Each location was included four or five times. Therefore, we spent 19 hours in total to measure at the four different locations. The measurements took place during a period of two weeks on different weekdays from Monday to Friday at the end of June/ beginning of July. All days were regular school days. An overview of all point measurements is given in Table 14.

4. Data Analysis

4.1. Station Data (Heidelberg, Berliner Straße)

Given a cyclist, cycling a certain route every day: How high would the annual mean NO_2 concentration be that he is exposed to? Of course, in order to get a mean concentration of NO_2, it is always best to measure the concentration as many times as possible. However, it was our aim to have an overview over many different places and streets in Heidelberg. Therefore, it was certainly not possible to just measure everywhere for several days, weeks or even months. Yet, the measurement station in Berliner Straße in Heidelberg measures NO_2 continuously. The data for hourly mean concentrations and annual mean concentrations of NO_2 can be accessed by the public on the official website of the agency. [9]

4.1.1. Extrapolation of Measurement Data to Annual Mean

Using the hourly mean concentrations from the measurement station at Berliner Straße from [9], we attempted to extrapolate annual mean concentrations from our measurement data according to (30). We assumed that the variation in NO_2 at the places of our measurements was the same as for the place where the environmental measurement station is situated. This assumption makes use of the fact that the weather conditions are about the same all over Heidelberg at a given time. Also, the peaks of the traffic volume during rush hours are assumed to be at the same time all over Heidelberg. If this assumption holds true, the measurements at either site deviate by the same factor from the respective annual mean of each site. With the measured NO_2 concentration at the local measurement site c_l, the annual NO_2 concentration at the local measurement site c_{aml}, the NO_2 concentration at the environmental station c_s measured at the same time and the annual mean concentration measured at the environmental station c_{ams} relate accordingly:

$$\frac{c_l}{c_{aml}} = \frac{c_s}{c_{ams}} \tag{29}$$

Of course we can flip the equation and extrapolate the annual mean NO_2 concentration at our measurement point

$$c_{aml} = c_l \frac{c_{ams}}{c_s} \tag{30}$$

However, this is only a rough approximation and is not perfect to evaluate the mean NO_2 concentration a cyclist or pedestrian is typically exposed to. The annual mean of the environmental station includes data measured during nights. But during these times there are fewer commuters on the road and also the typical NO_2 concentration on weekends differs from those on a typical workday. Additionally, we expected the seasons to play a role on the average NO_2 concentration.

4.1.2. Extrapolation of Measurement Data to Different Categories

The question is how we can find the best approximation of the NO_2 concentration a typical commuter cycling to his workplace is exposed to? In chapter 4.1.1 we saw how we can extrapolate our measurement data to mean values at the local measurement point for a whole year using equation (30). But in fact, we can extrapolate our measurement data to mean values of all different categories of different time intervals. Categories of interest might be different months, weekdays or certain times of the day.

Table 3 Meaning of the subscription of the various concentrations in (31)

Subscription	Meaning
'cml'	Mean concentration for the category 'c' at the local measurement site
'l'	Measured concentration at the local measurement site
's'	Measured concentration at the measurement station
'cms'	Mean concentration for the category 'c' at the measurement station
'ams'	Mean concentration over the whole year at the

	measurement station
'aml'	Mean concentration over the whole year at the local measurement site

Using all the subscripts explained in Table 3, we can use the extrapolated annual mean concentration to calculate the concentration at the local measurement site extrapolated to a mean value for a category of time that is of our interest:

$$c_{cml} = c_l \frac{c_{cms}}{c_s} = c_l \frac{c_{ams}}{c_s} \frac{c_{cms}}{c_{ams}} = c_{aml} \frac{c_{cms}}{c_{ams}} \tag{31}$$

The last step is quite useful as it makes us very flexible in transforming our measurement data to an extrapolated mean value of a certain category. In the first step we norm our data to an extrapolated annual mean. This makes our data independent of the time it was actually measured at. In the next step we can easily transform our data from the extrapolated annual mean to an extrapolated mean value of the category "c" by just multiplying the data by the coefficients c_{cms}/c_{ams}. Note that this way, if we want to extrapolate mean values for multiple categories, the times when the measurements were executed only need to be considered once.

The resulting coefficients c_{cms}/c_{ams} that one needs to convert our extrapolated annual mean values to a mean value of category „c" can be found in Table 17 and Table 18. They are based on the results of the next chapters 4.1.3, 4.1.4 and 4.1.5. In these chapters we analyse all the NO_2 concentrations measured by the environmental station from 01.08.2017 to 31.07.2018 and have a look on the effect of different parameters on the mean NO_2 concentration.

As we have this simple method to convert extrapolated annual mean values to extrapolated mean values of another category, we will only use the extrapolated annual values in the following. Unless stated differently, we will refer with "extrapolated data" or "extrapolated measurements" to the extrapolated annual mean values of our measurements.

4.1.3. Monthly Variation

First of all, we sorted the data by months, resulting in the variation of the NO_2 concentration in Figure 11. There is obviously a variation over the year, which is caused by a higher abundance of inversions in winter time than in summer time. Table 18 in the appendix contains the coefficients c_{cms}/c_{ams} that one needs to convert our extrapolated annual mean values to a mean value of each month.

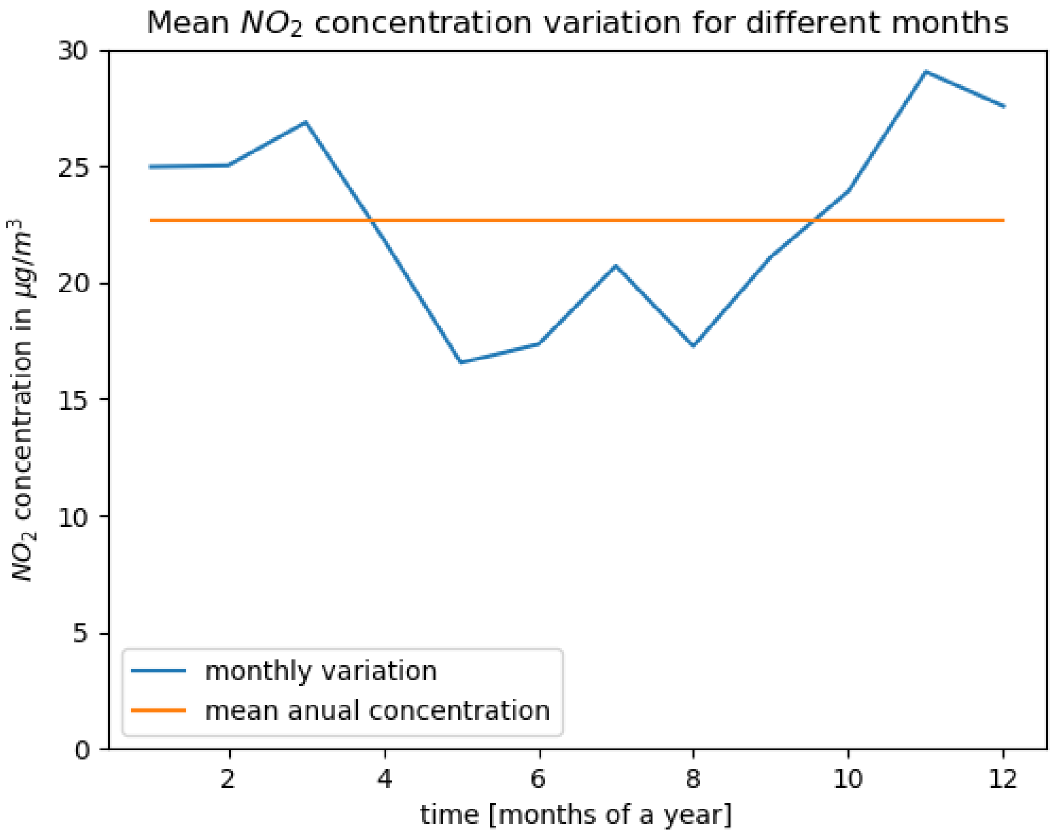

Figure 11 The variation of the NO_2 concentration at the environmental measurement station over one year. As a comparison the mean value of the corresponding time interval 01.08.2017 to 31.07.2018 is plotted as a line.

However, as we will see, the variation is less relevant compared to other parameters that we analyse further down.

4.1.4. School Holiday vs. School Time and Work Day vs. Weekend

Next, we sorted the data by the categories „school holidays“ or „school time“, „work day“ or „weekend and public holiday“ and the time of the day, while Saturdays are counted as part of the weekend. The result is presented in Figure 12. As one would expect, the mean values for days during school holidays are lower than the corresponding values during school time. However, the most significant effect is due to weekends and normal workdays during the daytime. On normal workdays, the NO_2 concentration rises enormously over the morning and a little less over the afternoon. As long school holidays in Germany are during summer time, we should keep in mind that the category "school time” contains a higher proportion of winter days than the category “school holidays”. Therefore, not only a change in the traffic volume but also seasonal effects may cause the differences between school time and holidays. Table 17 in the appendix contains the coefficients $\mathrm{c_{cms}}/\mathrm{c_{ams}}$ that one needs to convert our extrapolated annual mean values to the mean values for the categories “school time” or “school holidays” and “workday” or “weekend” for all hours of a day. The values in the columns „Std.“ contain the standard deviation of the values that were taken into account to calculate c_{cms} divided by the annual mean concentration at the station, c_{ams}.

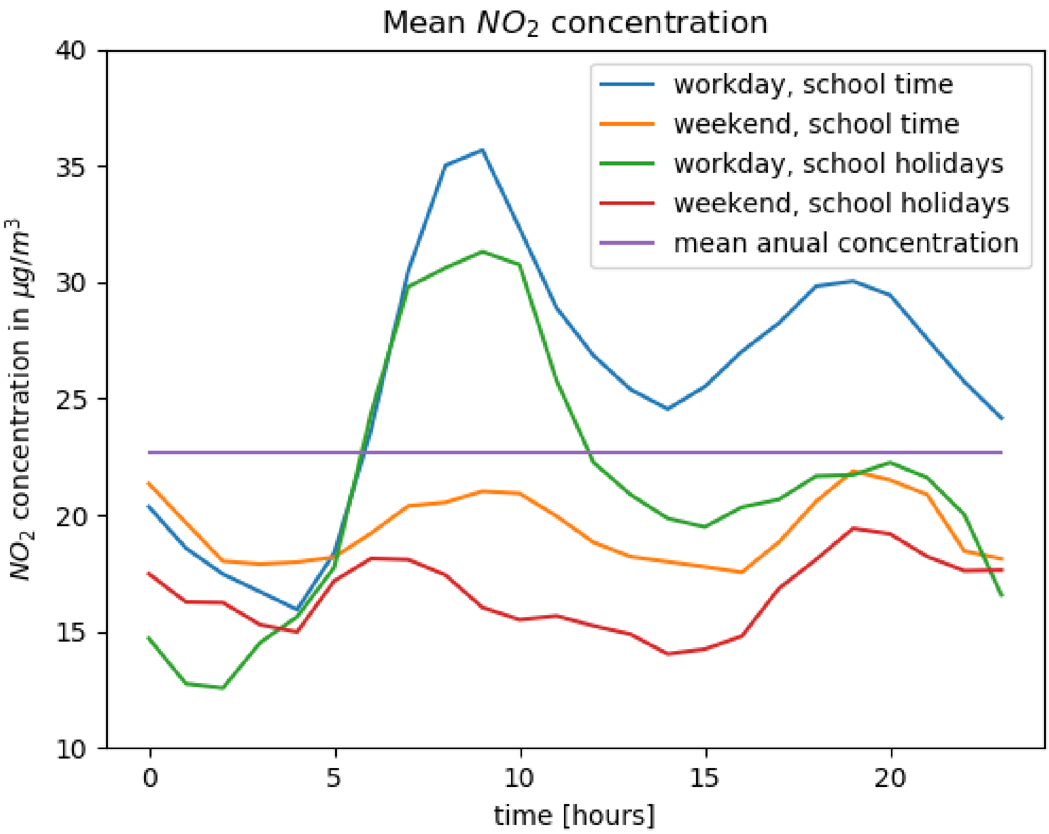

Figure 12 Mean variation in NO_2 for the categories "workday" or "weekend" during "school time" or "school holidays". As a comparison the mean value of the corresponding time interval 01.08.2017 to 31.07.2018 is plotted as a line.

4.1.5. School Time vs. School Holidays for all Weekdays

To have an even closer look into the variation in NO_2, we now sorted the NO_2 measurements by all weekdays. We wanted to check whether the NO_2 concentration differs significantly e.g. on a Monday compared to a Wednesday. Additionally, we still sorted the data into school holidays and school days. The result during the school time is plotted in Figure 13. Due to the many categories we now sort the data by, the mean values are now based on only few one hour mean concentrations. Some mean values consist of less than 40 one hour mean concentrations. Special weather conditions during certain days throughout the year are now more likely to influence our curves. Therefore, we do not consider the variations between the days Monday to Friday to be on a significant scale. On the contrary, the variation between these days and Sundays is definitely significant. The NO_2 concentrations on Saturdays are in between. Taking into account that a huge part of the commuters only go to work from Monday to Friday, some go to work (and others go shopping) on Saturdays and almost none go to work on Sundays, the curves in Figure 13 seem to be reasonable. Whether Saturdays should count as "workdays" or "weekend" can be discussed for sure. We decided to count it as a day of the category "weekend" in Figure 12. This way, we only have two categories, and at the same time the coefficients for the workdays Monday to Friday (that most people go to work at) will not be underestimated.

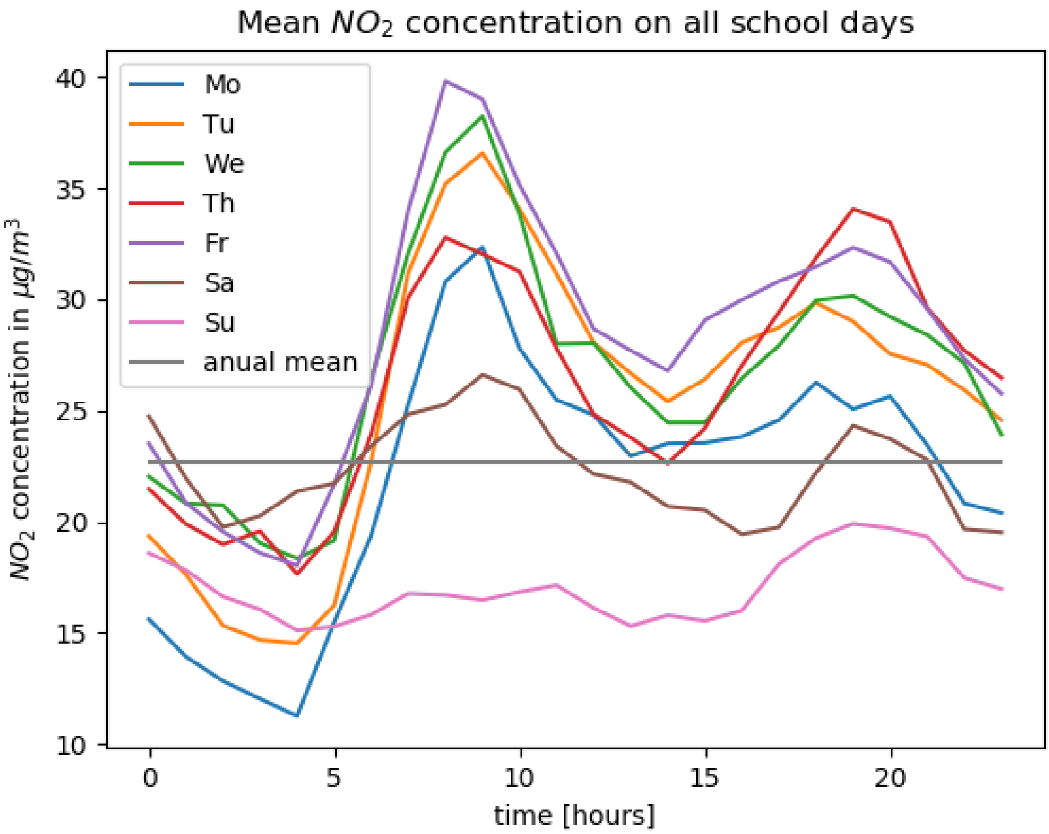

Figure 13 Mean diurnal variations in NO_2 for all weekdays during school time. As a comparison the mean value of the corresponding time interval 01.08.2017 to 31.07.2018 is plotted as a line.

We therefore conclude that the most important factors for a variation of the NO_2 concentration are the time of the day and whether the measurement takes place on a weekend or a workday. The effect of school holidays and school time is also clearly visible, even though the magnitude of the variation is lower.

4.2.Station Data Background (Schwäbische Alb)

In the chapter "Station Data (Heidelberg, Berliner Straße)" we have analysed the variation of the monthly mean values over the year. At this point we would like to figure out to which extent this variation depends on the city and to which extend this variation can be found in rural areas in the same way. We therefore take monthly mean concentrations of NO_2 from the LUBW for a background measurement station at the Schwäbische Alb, Erpfingen from [9]. The air-line distance from the station to Heidelberg is about 120km. Still it is the next background measurement station we could find. Using all monthly means from January 2000 to December 2017 (no later data available) we get the variation plotted in Figure 14. It looks quite similar to Figure 11. Note that the monthly mean in Figure 11 is based only on one year and therefore the curve is not as smooth as in Figure 14. For the measurement station in Heidelberg the absolute difference between the highest monthly average and the lowest monthly average is 12.5 $\mu g/m^3$ (55% of annual mean in Heidelberg), while it is 7.6$\mu g/m^3$ (105% of the annual mean in Erpfingen) at the background measurement station in Erpfingen. This means that more than half of the variation of the monthly mean NO_2 concentrations in Heidelberg is caused by the variation of the background NO_2 concentration. Only a smaller part is caused by for example a seasonal variation of the traffic volume or more NO_2 emissions by heating systems in winter than in summer. Of course, for this we need to assume that at the measurement station close to Erpfingen, the measurements are not affected by traffic and heating systems.

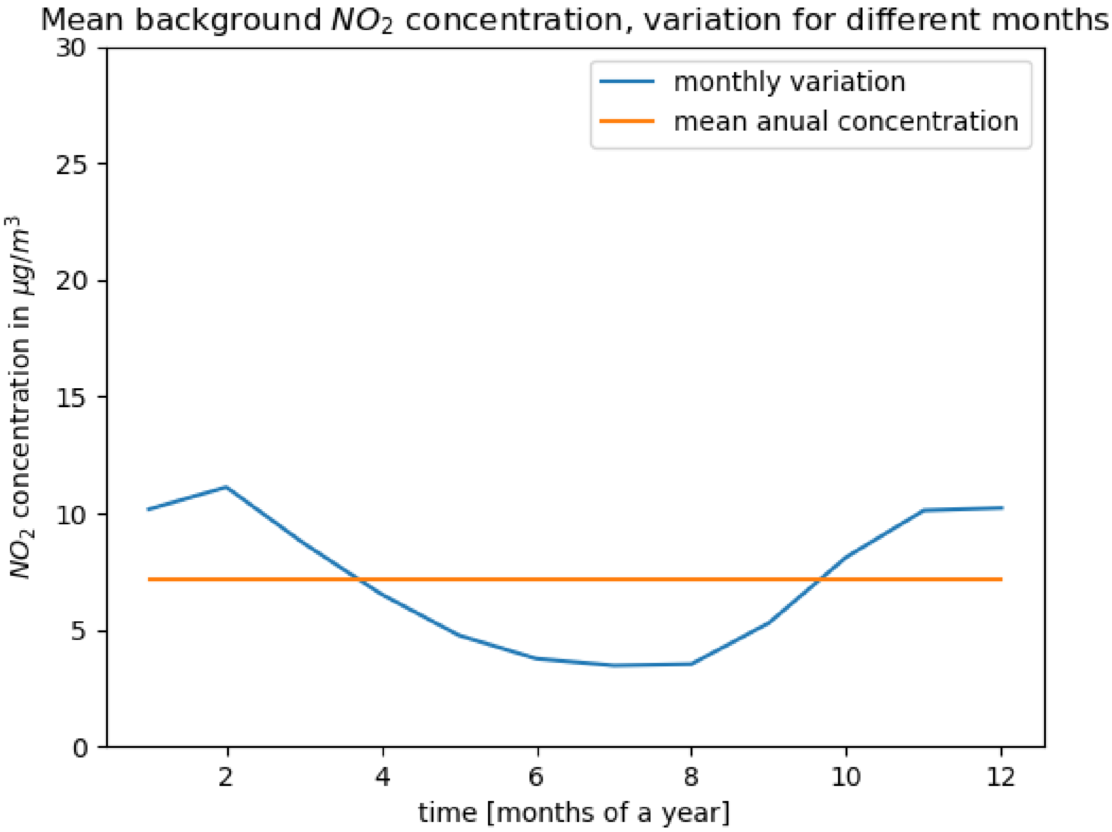

Figure 14 Background NO_2 concentration. Measured data from measurement station in Erpfingen from January 2000 till December 2017. The annual mean is $7.2\mu g/m^3$.

4.3.Spatial Mean

To draw conclusions about the pollution of the whole route we would like to find something like an average NO_2 concentration of the whole route. However, if we just took the average of all our single measurements, the value would strongly depend on the time we spent in certain streets or places. The longer we stayed in a street with only little NO_2 in the air, the lower this average would become. On the contrary, if we stayed in a highly polluted street, the average would be higher. To make sure that our results do not depend on any such effects, we will calculate the "spatial mean" as described in the following and visualised in Figure 15.

To get an overview, we join the data from all runs available of the category that is to be analysed and sort them into a grid of little squares in longitude and latitude so that the whole route is covered by the grid. Each square consists of an interval of about 0.0007° in longitude and 0.0004° in latitude. This corresponds to a square of about 45 meters on either side. For each square in the grid we calculated the mean NO_2 concentration and the standard deviation. This is visualised in Figure 15. We assign a GPS position to each square and its mean NO_2 concentration. This is obtained by averaging the longitude and latitude values of the measurement points in the square. This way it is more likely that the final mean value of a square will be placed on the street and not on a building next to it. Additionally, we count the number of measurements per square to assure that the resulting mean of one square does not consist of only very few data points (and hence is not very reliable). In case there are less than 10 data points in a square, we will not provide a valid NO_2 value in the square, as it is not representative. We call this resulting data set of mean values the “spatial mean”. Finally, to get an overview of the whole route, we take the mean of this dataset. We will call the resulting mean NO_2 concentration of the spatial mean the “global spatial mean” of our route. Note that this value, of course, is not the average value for Heidelberg as it strongly depends on the composition of the route. If we had included more field paths into our route, it obviously would have been lower. Also, it still depends on the number of runs we executed during off peak time versus the number of tours we executed during peak time as long as we use the data of all measurements. However, we can use it as a reference when comparing different parts of the route or assessing the quality of our extrapolation method.

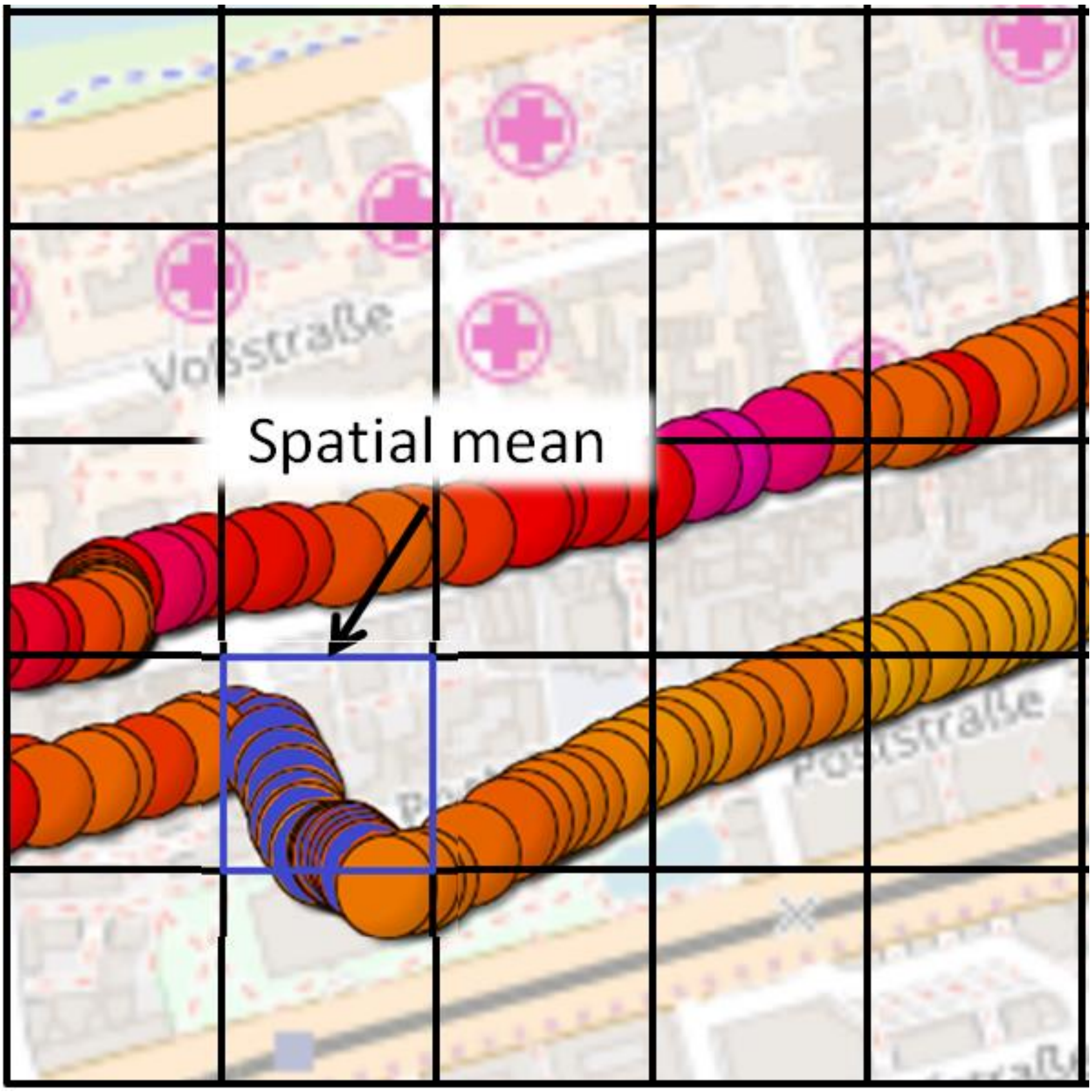

Figure 15 Schematic representation of a spatial mean value and the global spatial mean. The spatial mean is the average of all measurements in e.g. the green square. The global spatial mean is the mean value of all spatial mean values within the blue square. For a better overview in this example only a part of the route is covered by the global spatial mean.

5. Results

5.1. Route Measurements

5.1.1 Measured NO_2 concentrations

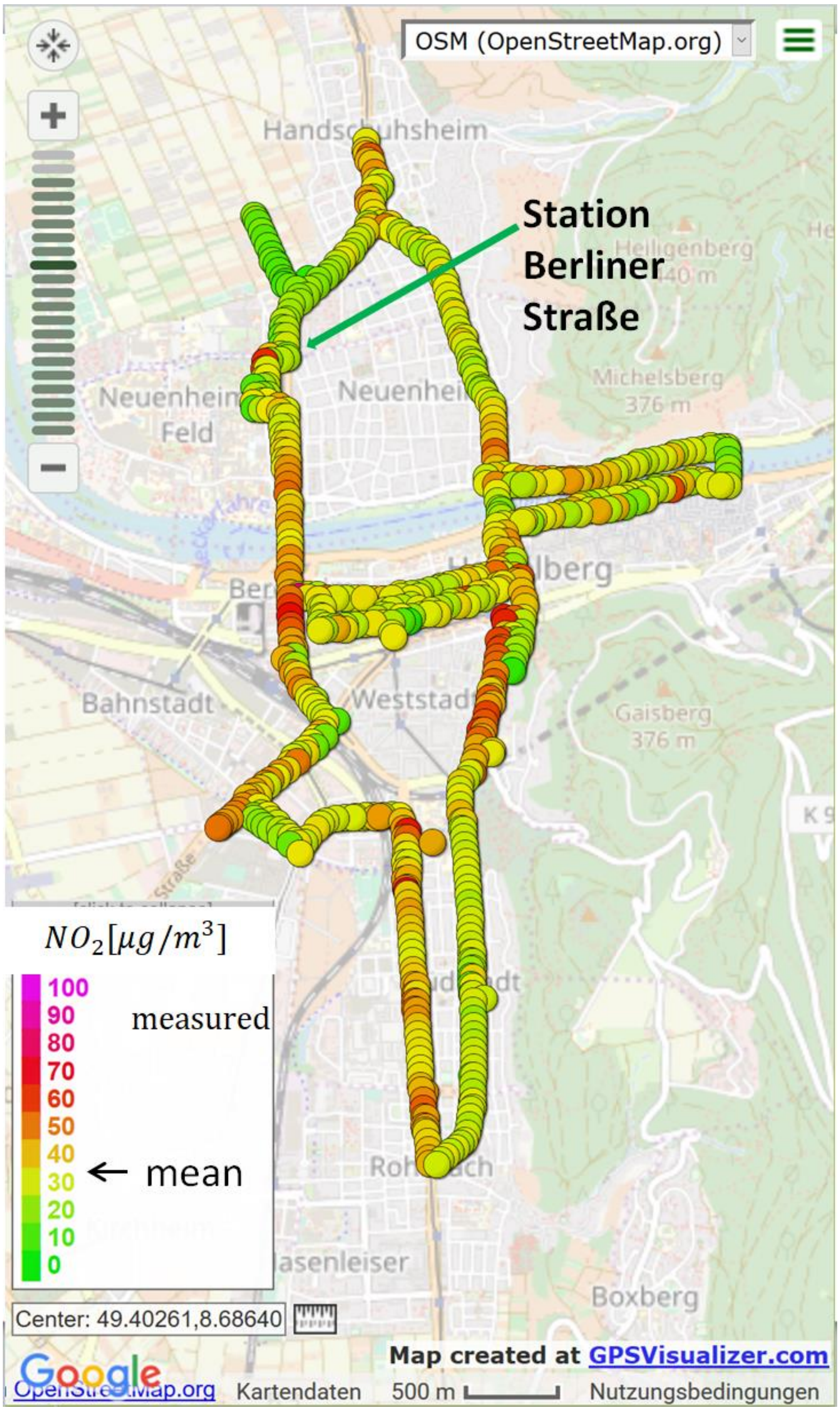

Figure 16 Spatial mean of all measurements except point measurements. Only mean values that consist of at least ten data points are included.

To get an overview, we calculate the spatial mean based on all measurements as described in the chapter "Spatial Mean" and plot it in Figure 16. Averaging all spatial data we get a total mean of

$33\mu g/m^3$, as can be seen in the bar chart in Figure 20 or in Table 4. Note that this data contains off-peak as well as peak measurements, as we use all measurement runs that were executed on the route.

5.1.1.1 Comparison of Summer versus Winter Measurements

To have a closer look on the differences in the NO_2 concentration between summer and winter, we split the data into summer and winter measurements and again calculate the spatial mean of our measurements. As presented in Figure 20, we get a global spatial mean of $40\mu g/m^3$ and a standard deviation of $12\mu g/m^3$for the winter measurements. For the measurements executed in summer time, we get a global spatial mean of $32\mu g/m^3$ and a standard deviation of about $11\mu g/m^3$. The question is whether all over Heidelberg the pollution is higher in winter time than in summer time in a similar way. To check the changes in the distribution of the NO_2 pollution, we plot the spatial mean for winter and for summer in Figure 17a and Figure 17b. Note that we adjusted the scale of the winter measurements to a range of $10\mu g/m^3$ to $110\mu g/m^3$ to allow a better comparison between both seasons.

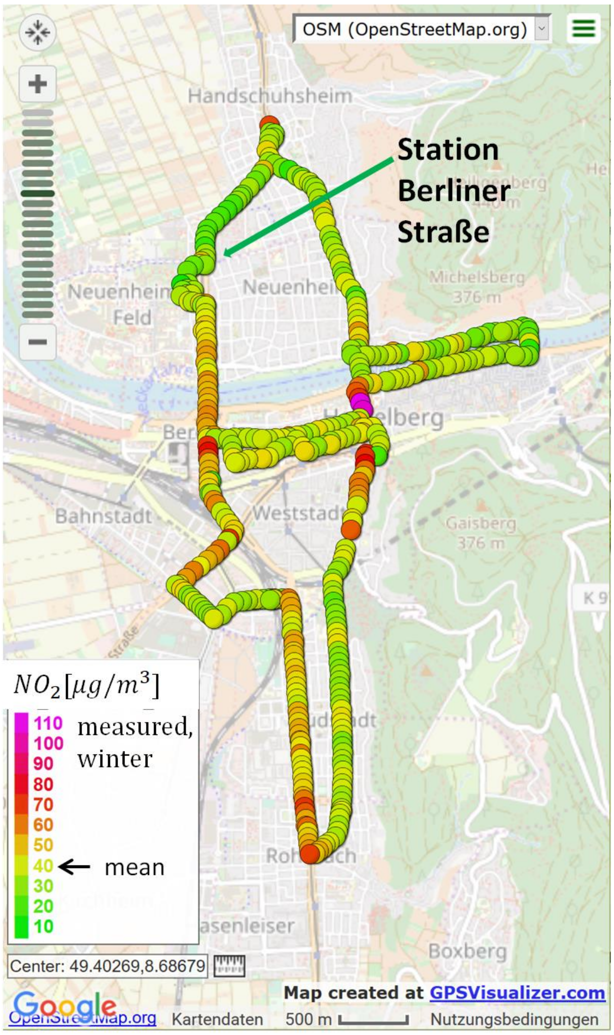

Figure 17a Winter, adjusted scale

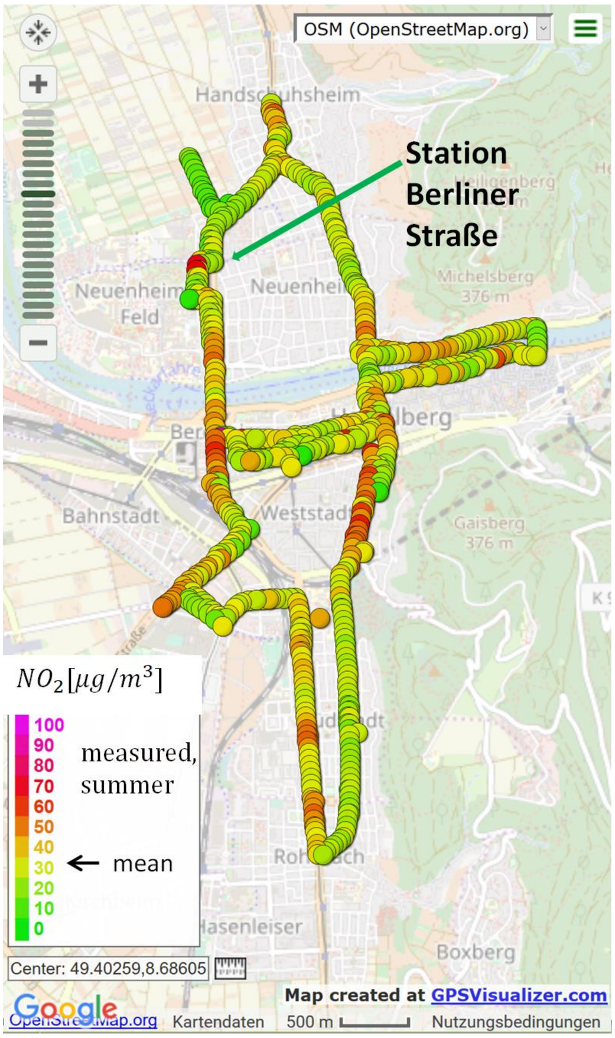

Figure 17b Summer

Figure 17 Spatial mean of all measurements except point measurements split into measurements executed in summer and winter time. Only mean values that consist of at least ten data points are included. The global spatial mean is marked in the legend.

As we can see, the distribution is similar all over Heidelberg for both seasons. Exceptions can be found in the very south of the route at Rohrbach Markt (south end of street 19 in Figure 8), where the NO_2 concentration seems to be lower in summer than in winter relative to the global spatial mean of the respective season. Also, Bismarckplatz (see Figure 9 in Figure 8) seems to have lower concentrations relative to the mean. On the other hand, Brückenstraße (street number 6 in Figure 8) seems to be higher polluted in summer. However, we should keep in mind that single data points for the spatial mean can fluctuate if, by chance, single measurements in this area took place in the plume of a strong emitter like a bus. The plots of the summer route also picture data points for the field path in the top left hand part (street 2 in Figure 8). As this field path was added to the route in summer for a better check on the background NO_2 concentration around Heidelberg, there are no data points for the winter season. As this only adds a small number of single data points to the spatial mean, this will only have little influence on the global spatial mean and hence only little influence on the plots in Figure 17.

5.1.2 Extrapolated NO_2 concentrations

In Figure 18 we plot the spatial mean for the whole route again. The plot is based on the extrapolated annual mean values, using (30) for each single measurement data point. Afterwards, all of these extrapolated annual mean data points are averaged to spatial means according to chapter 4.1.3. This way we can get a better overview about where in Heidelberg we expect the official threshold of $40\mu g/m^3$ to be exceeded in the annual mean. Interestingly, the global spatial mean of our extrapolated annual NO_2 concentrations (excluding the data of our point measurements) is exactly $40\mu g/m^3$ with a standard deviation of $21\mu g/m^3$ according to Table 4 and the bar chart in Figure 20. As this is only the mean value and the concentration is not constant everywhere, we find numerous parts of Heidelberg in Figure 18 where the threshold is exceeded. However, this does not mean that a measurement station at these locations would exceed the threshold, as the cycling measurements are much closer to the traffic.

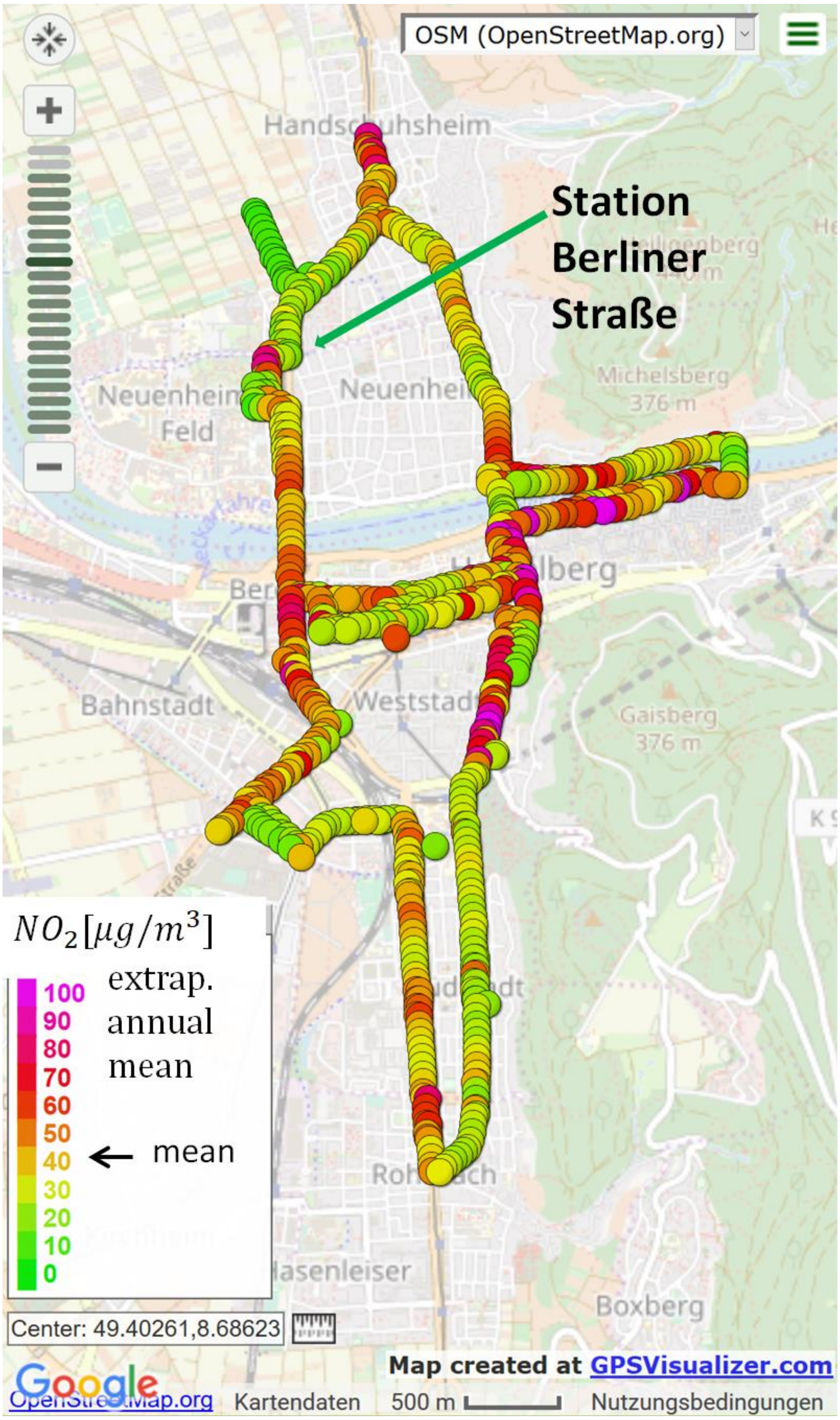

Figure 18 Spatial mean of all extrapolated annual mean measurement points except point measurements. Only mean values that consist of at least ten data points are included.

5.1.2.1 Comparison of Extrapolated Annual Mean from Summer versus Winter Measurements

Again, we would like to have a closer look on the differences of the extrapolated NO_2 concentration in the winter and summer season on the map of our route. Therefore, we separate the measurement data that was extrapolated according to (30) into summer and winter data and plot it separately. We find a global spatial mean for the extrapolated annual mean from the summer data of $43\mu g/m^3$ with a standard deviation of $23\mu g/m^3$. For the winter data we find a global spatial mean of $28\mu g/m^3$ with a standard deviation of $7\mu g/m^3$. The extrapolated spatial mean is plotted in Figure 19a and Figure 19b. To allow a better comparison, we adjusted the scale for the summer data.

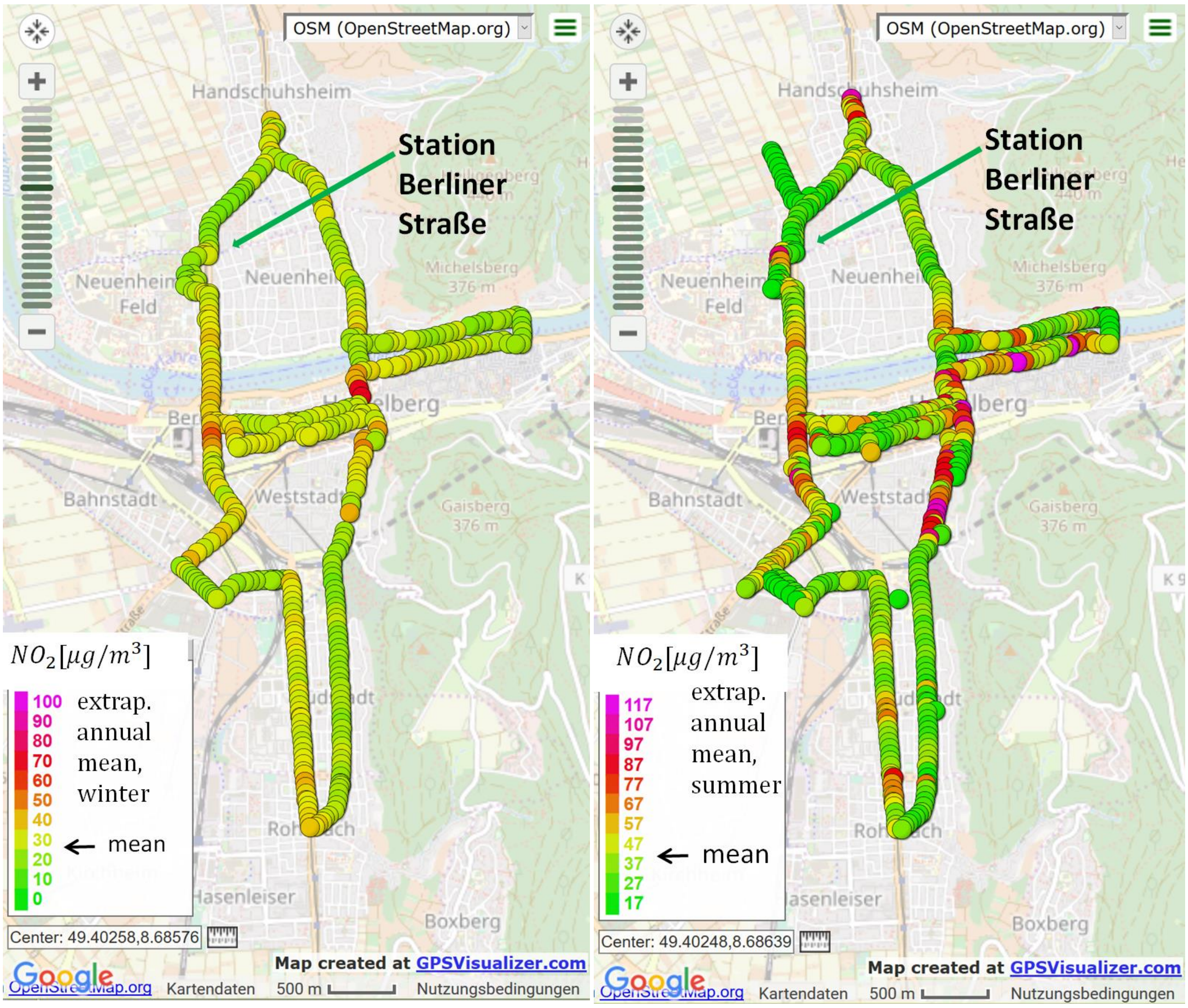

Figure 19a Winter

Figure 19b Summer, adjusted scale

Figure 19 Comparison of extrapolated annual mean in summer versus winter. The data is normed by the total mean of the extrapolated summer means and the extrapolated winter means respectively. Again only mean values that consist of at least ten data points are included. For a better comparison the scale for the summer data was adjusted.

In contrast to the comparison of the spatial mean for the measured data, the extrapolated data presents some more significant differences. According to the plots in the south of the route, Römerstraße (number 8 in Figure 8) is less polluted in summer relative to the total mean of the respective season. The same effect can be observed for the small side roads in the south of Bergheimer Straße (number 11 in Figure 8) as for example the (number 23 in Figure 8) or Alte Eppelheimer Straße (number 25 in Figure 8). On the other hand, Brückenstraße (number 6 in Figure

8) and some parts along the river bank as well as the north of Rohrbacher Straße (number 21 in Figure 8) are higher polluted in summer in comparison to the total mean.

5.1.3 Comparison of Measured NO2 concentrations versus extrapolated annual mean NO2 concentrations

It is also remarkable that the global spatial mean of the extrapolated annual mean from the winter measurement data is lower than the global spatial mean of the extrapolated annual mean based on the summer data. However, for the global spatial mean of the measured mean concentrations, the situation is reversed: The mean in winter is higher than in summer. Furthermore the extrapolated annual mean values fluctuate stronger than the measured mean values. The extrapolated annual mean from the winter measurements is lower than the measured mean concentration in summer and vice versa. An overview is given in Figure 20 and Table 4. The reasons for this will be further discussed in chapter 5.3.

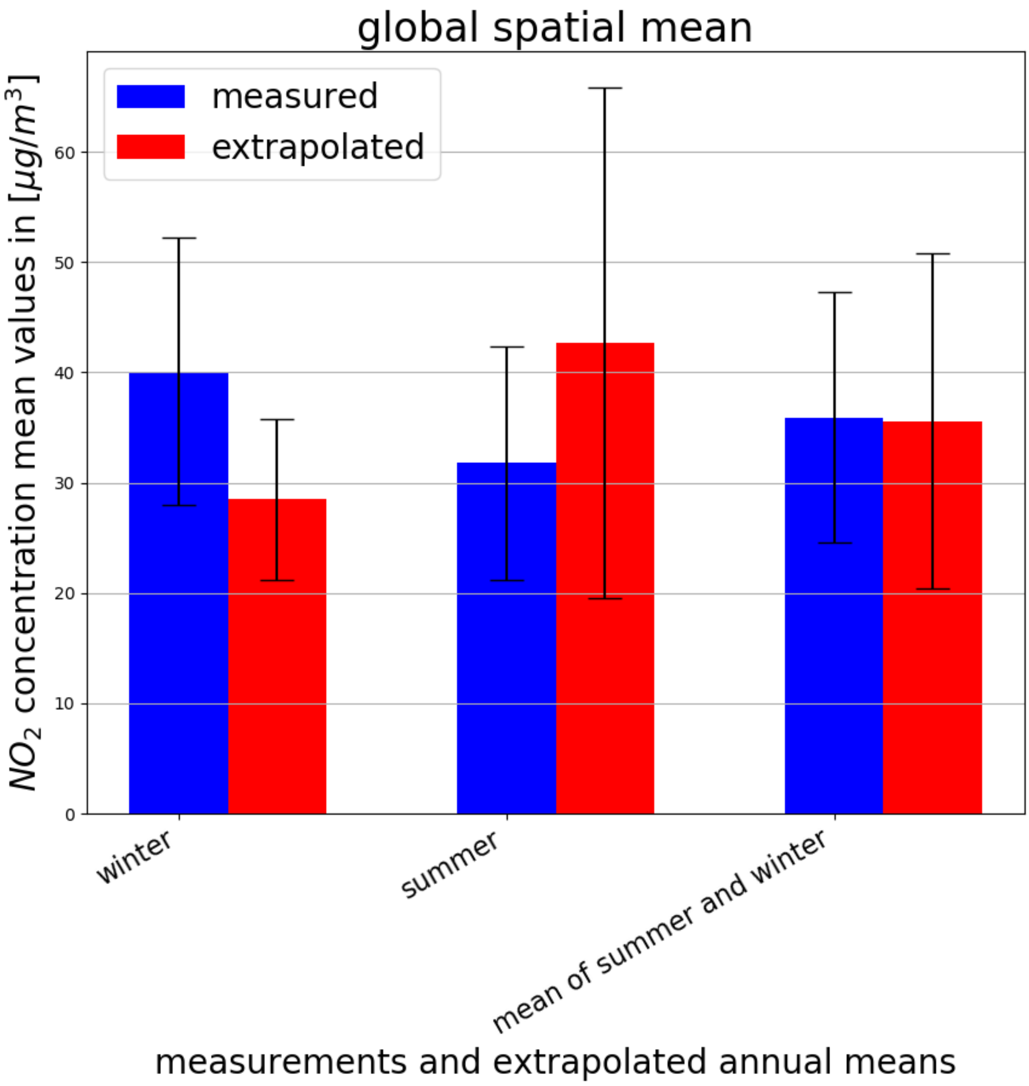

Figure 20 Comparison of mean from measurement data (except point measurements) to mean of extrapolated annual mean. The comparison is done for all data as well as for data collected in winter and summer time separately. The error bars represent the standard deviation of the measurement data and not the uncertainty of our measurements. Peak and

off-peak measurements are not distinguished here. The red bars for winter and summer represent the extrapolated annual mean based on the measurement data of only the respective season.

Table 4 Mean NO_2 concentrations and standard deviation for global spatial mean values.

	All measurements $[\mu g/m^3]$		Winter $[\mu g/m^3]$		Summer $[\mu g/m^3]$		Mean of Summer and Winter in $[\mu g/m^3]$	
	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std.
Measured	33	10	40	12	32	11	36	11
Extrapolated	40	21	28	7	43	23	36	15

5.1.4 Comparison of Peak versus Off-peak Measurements

We will have a look on the differences between peak and off-peak measurements. We considered a measurement to be a peak measurement if it took place from Monday to Friday, 7:00 to 10:00 or 15:00 to 18:00. On the contrary, off-peak measurements were executed on Sundays. To be independent of fluctuations that we observed in the extrapolated data for example in chapter 5.1.3, will only look on the measured data. However, this also means that our results depend on the actual weather conditions of our measurement runs. As only few winter measurements covered the whole route and for both, summer and winter, we only have few off-peak measurements we cannot use the total mean of the spatial mean. Many squares do not have enough data points to reach the threshold of ten data points and are therefore not considered in the spatial mean calculation explained in 4.3. We will therefore simply use the mean value of the measurements that are considered in this chapter. The influence this has on our results is analysed in chapter 5.1.2. For the measurements in summer we will only consider the measurement runs that covered the whole route and were executed with no break. For wintertime we have not enough measurement runs that fulfil these conditions. Therefore, for wintertime we need to use all runs, even though not all runs cover the whole route. Despite these circumstances the results are interesting to look at.

In Figure 21 we plotted the resulting mean values of our peak and off-peak measurements given in Table 5. The green bars represent the off-peak measurements, based only on the measurement runs 7 and 8 for winter time and 12, 24 and 35 for summer time (see Table 13 in appendix). As we expected after the analysis of the background NO_2 concentration in chapter 4.2, the off-peak measurements in winter show slightly higher concentrations than in summer, but generally are almost constant for the different seasons. On the contrary, the peak measurements show a strong fluctuation. In winter the NO_2 concentrations are $15\mu g/m^3$higher than in summer. This result is based on the runs 1 to 6 (only runs 5 and 6 cover the whole route) for the winter time and runs 10, 11, 13, 15, 16, 18, 19, 21, 23, 29 and 31 for summer time (see Table 13 in appendix). The difference in the mean concentration could be explained by thermal inversions that occur more often in winter than in summer time.

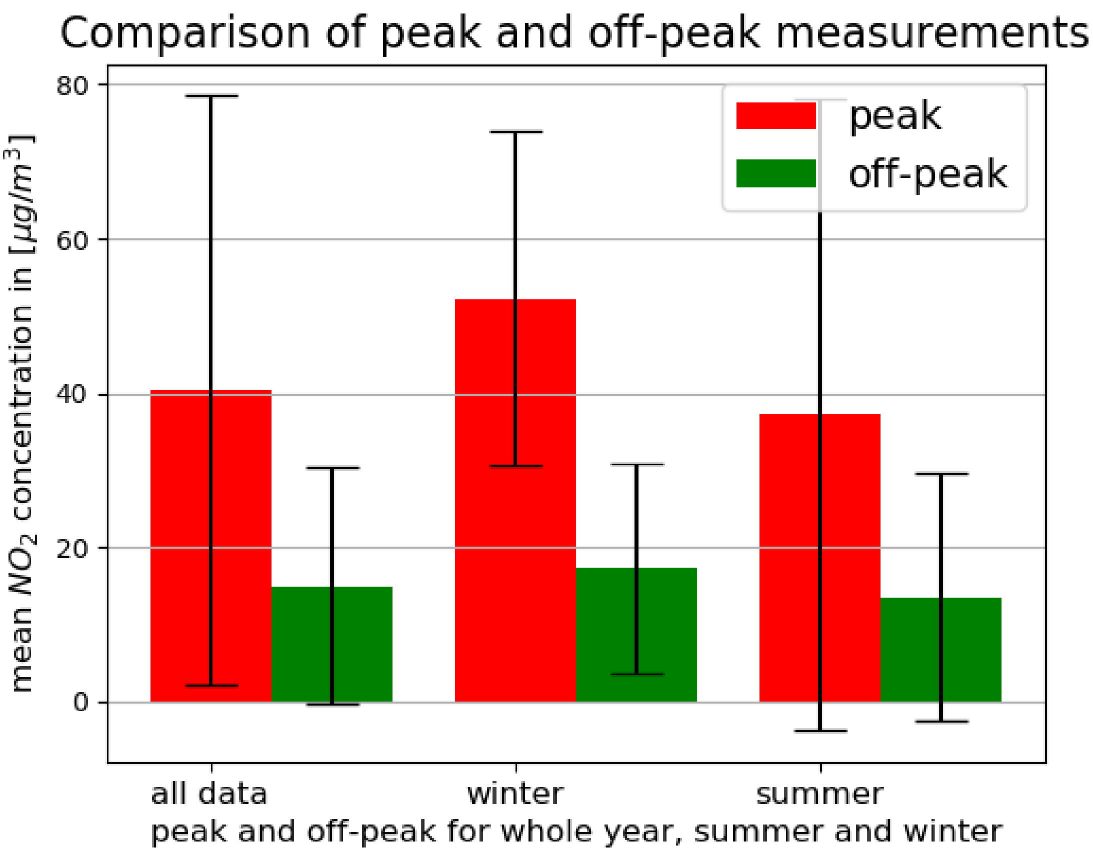

Figure 21 Comparison of peak and off-peak measurements. The error bars represent the standard deviation and not the error of our measurements. For summer time only measurement runs covering the whole route with no breaks in between are considered to have as small variations as possible in the NO_2 concentrations caused by changing weather conditions and different daytimes.

Table 5 Comparison of peak and off-peak measurements. For summer time only measurement runs covering the whole route with no breaks in between are considered.

	Peak $[\mu g/m^3]$		Off-peak $[\mu g/m^3]$	
	Mean	Std.	Mean	Std.
All data	40	38	15	15
Winter	52	22	17	14
Summer	37	41	14	16

5.1.5 Measurements in the Area of the Measurement Station

Table 6 Comparison of annual mean from station to mean of our measurements as well as our extrapolated annual means in the area around the station. For Mittermaierstraße the bicycle measurements took place on the side of the road opposite the passive sampler. For both stations two areas of different size have been analysed.

Location	Annual mean measured by station $[\mu g/m^3]$	Number of data points considered next to station	Mean measured concentration in $[\mu g/m^3]$ and in brackets the deviation from station in [%]	Extrapolated annual mean of our measurements in $[\mu g/m^3]$ and in brackets the deviation from station in [%]

Berliner Straße	24	756	25 (4%)	19 (19%)
	24	2505	24 (0%)	22 (7%)
Mittermaierstraße (opposite side of the road)	39	101	65 (66%)	80 (105%)
	39	364	60 (53%)	76 (95%)

Another interesting question is how the average of the measured concentration and the average of the extrapolated annual mean concentration just next to the measurement station fit with the annual mean of the environmental measurement station in Berliner Straße and the passive sampler point at Mittermaierstraße. An overview of the results can be found in Table 6. For the mean of the measured data we find a concentration of $25\mu g/m^3$ in the closest square from our spatial mean grid (see chapter 4.3). This includes all measurements in a range of 45 meters around the measurement station. For the extrapolated measurement data the closest square has a value of $19\ \mu g/m^3$. This square contains 756 single measurements. If we include all measurements within a maximum distance of 90 meters to the measurement station (this corresponds to the three closest squares), we have a set of 2520 single measurements. The mean of the measurements in these three squares gives a mean value of $24\mu g/m^3$ for the measured data with a standard deviation of $22\mu g/m^3$. The respective mean value for the extrapolated annual mean is $22\mu g/m^3$ with a standard deviation of $16\mu g/m^3$for the extrapolated measurements respectively. The measurement station itself measured an annual mean value for 2017 of $24\mu g/m^3$. [10] Considering the four squares closest to the measurement station, the average of our measured NO_2 concentration is the same as the one from the station and the average of the extrapolated annual mean value varies by 7%.

The second measurement station that only publishes annual mean values is the spot-measurement station at Mittermaierstraße. For 2017 the annual mean concentration was $39\mu g/m^3$. [10] As this measurement station is not situated at a crossing and we did not perform point measurements in front of this measurement station, only a total of 364 single measurements within a range of 90 meters around the passive sampler (this corresponds to three squares of our spatial mean grid) are available next to the measurement station. The measurements were measured on the side of the road opposite from the passive sampler. The average of these 364 measurementss is about $60\mu g/m^3$ with a standard deviation of $27\mu g/m^3$. The average of extrapolated annual mean values of these measurements is even higher. Here we find an average of $76\mu g/m^3$ with a standard deviation of $54\mu g/m^3$. This is impressive in several ways.

First, neither the average of our extrapolated annual mean values nor the mean of these measurements itself fit to the annual mean value measured by the spot-measurement station in Mittermaierstraße. They exceed the annual mean value measured by the station and deviate by 53% and 95% respectively. At the same time, the high deviation of our mean value for the measured data is astonishing, since at Berliner Straße the values fitted very well.

The second reason why these deviations are impressive is that all average values – the annual mean from the station at Mittermaierstraße, our own mean of the measured values and the mean of the extrapolated values – are very high. As seen in Figure 16, this place is one of the most polluted places on our measurement route. However, at least on one side of the road we can find rather high buildings and the distance between the street lanes and the houses is just wide enough for a pavement for pedestrians and a bikepath for cyclists on either side. Therefore, the buildings form a street canyon with a high traffic volume.

5.1.6 Individual Streets

To have a closer look at our measurement data, we split all our data points into the streets that they belong to. Then we calculate the mean NO_2 concentration and standard deviation for the measured data as well as for the extrapolated data separately for each street. The resulting mean NO_2 concentrations are found in Table 7 and in the bar chart in Figure 22. In Figure 22 the error bars represent the standard deviation and not the error of the measurements. Also, it is important to remember that the data on which the mean values are based might have been measured at different conditions and not equally often, as not all measurement runs covered the whole route. Again, data from point measurements is not considered. This is because, due to the long measurement times at certain spots compared to a usual run, these data points would have a disproportionately high weight and the mean value would no longer represent a mean value over the different runs for the streets in which the point measurements took place.

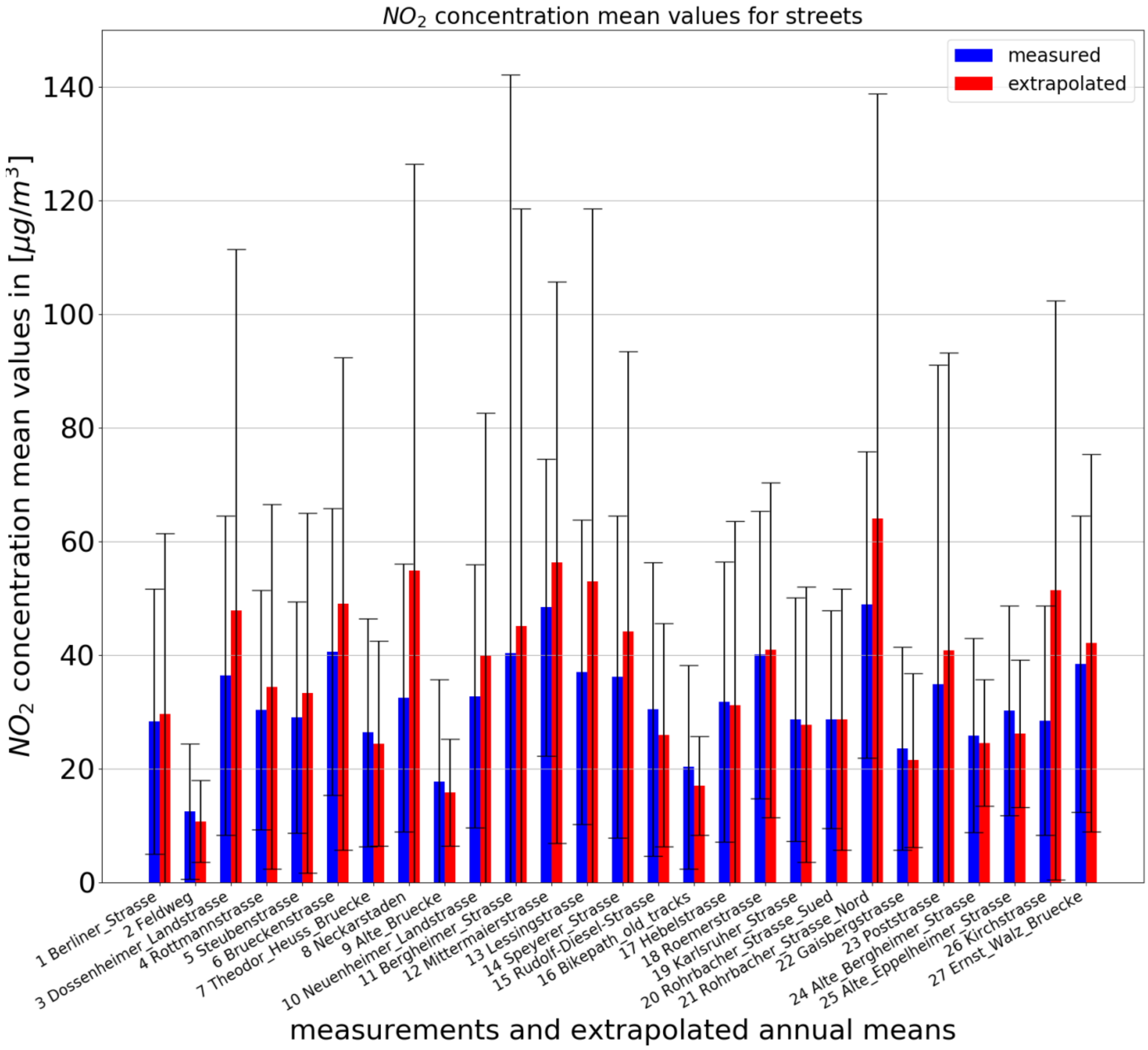

Figure 22 Mean NO2 concentrations for all streets. Mean values for measured data in blue and extrapolated data in red. The error bars represent the standard deviation (and not the error) of the data points for each street.

Table 7 Mean NO2 concentrations of the measurements in the streets included in route (see Figure 8 for a map with the streets)

Street number	Street name	Mean measured concentration $[\mu g/m^3]$		Annual mean (extrapolated) $[\mu g/m^3]$		Number of data points
		Mean	Std.	Mean	Std.	
1	Berliner Straße	28	23	30	32	9150
2	Field path	12	12	11	7	867
3	Dossenheimer Landstraße	36	28	48	64	2588
4	Rottmannstraße	30	21	34	32	969
5	Steubenstraße	29	20	33	32	2047
6	Brückenstraße	41	25	49	43	1554
7	Theodor Heuss bridge	26	20	24	18	703
8	Neckarstaden	33	24	55	72	3380
9	Alte Brücke (old bridge)	18	18	16	9	844
10	Neuenheimer Landstraße	33	23	40	43	2256
11	Bergheimer Straße	40	102	45	74	3230

12	Mittermaierstraße	48	26	56	49	2949
13	Lessingstraße	37	27	53	66	1237
14	Speyerer Straße	36	28	44	49	2948
15	Rudolf-Diesel-Straße	30	26	26	20	1027
16	Bike path along old tracks	20	18	17	9	708
17	Hebelstraße	32	25	31	32	2113
18	Römerstraße	40	25	41	30	5127
19	Karlsruher Straße	29	21	28	24	1298
20	Rohrbacher Straße (south)	29	19	29	23	2612
21	Rohrbacher Straße (north)	49	27	64	75	1784
22	Gaisbergstraße	24	18	22	15	311
23	Poststraße	35	56	41	52	931
24	Alte Bergheimer Straße	26	17	25	11	187
25	Alte Eppelheimer Straße	30	18	26	13	437
26	Kirchstraße	28	20	51	51	642
27	Ernst Walz bridge	38	26	42	33	483

5.1.6.1 Evaluation of the NO_2 Concentrations

First we can have a look on the NO_2 concentrations themselves. In Table 8 we have the list with all the streets of our measurements, sorted by the mean measured NO_2 concentration. The table shows that the streets with no traffic as the field path, the bike track along the old tracks and the old bridge are the cleanest streets on our measurement route. Additionally, two of three bridges are among the streets with the lowest NO_2 concentration. However, the Ernst Walz bridge (street number 27) is among the six most polluted streets. This is surprising as most of the time it is rather windy on the bridge. But the bridge is highly frequented with cars and therefore, depending on the wind direction, the cyclists are simply in the plume of the cars next by. The difference to the Theodor Heuss bridge (street number 7) can either be explained by the difference in the traffic flow (most likely there were more cars waiting for a green traffic light at the Ernst Walz bridge than on the Theodor Heuss bridge) or by the different sides of the bridge we measured. Most times we passed the Theodor Heuss bridge on the west side, whereas we passed the Ernst Walz bridge on the east side.

On the other side of our ranking with high NO_2 concentrations, we find the streets with high or medium traffic volume. The nine most polluted streets are labelled with a high or medium traffic volume. The two most polluted streets are Mittermaierstraße (street number 12 in Figure 8, $48\mu g/m^3$) and the north part of Rohrbacher Straße (street number 21 in Figure 8, $49\mu g/m^3$).

5.1.6.2 Standard Deviation of Measurements

We should have a look on the standard deviation bars for the different streets in Figure 22. In comparison to the standard deviation bars in Figure 20, here, the standard deviation for some roads is much higher. It sometimes even exceeds the mean value itself for the respective road.

On the example of Bergheimer Straße (number 11 in Figure 8) we will analyse the reason for the extremely high standard deviation. For this road we have about 3200 sample points. Only three streets have even more sample points, so the statistical fluctuations of the standard deviation due to specific data points should be comparatively low. Since on Bergheimer Straße we can find trucks and busses but no separated bike path we sort the NO_2 concentrations and search for extremely high values. Indeed we find ten data points exceeding $670\mu g/m^3$ measured all during the same measurement run during the same minute. Additional ten data points exceed $290\mu g/m^3$, this time not measured during the same measurement run. There is no doubt that these very high concentrations were caused by a vehicle driving just in front of the bike. Indeed, on the pictures of our camera we find that the measurements with the highest ten values were taken at the end of Bergheimer Straße in the queue in front of a traffic light. On the corresponding pictures we can see a minibus waiting on the lane next to us and then overtaking when the lights turn green. If we exclude only these ten data points from our data set for the mean values and standard deviation, we find a new mean NO_2 concentration of about $35\mu g/m^3$ (formerly $40\mu g/m^3$) and a standard deviation of only $34\mu g/m^3$ (formerly $102\mu g/m^3$). If we exclude further ten data points with the highest values the mean NO_2 concentration decreases by only $1\mu g/m^3$ but the standard deviation decreases by further $9\mu g/m^3$, down to 25 $\mu g/m^3$.

As we could demonstrate with this example, even though we have many data points for each street, the high standard deviation is caused mainly by single vehicles with exceptionally high NO_2 emissions. Therefore streets with no or little traffic as for example the field path (street number 2 in Figure 8) or the bike path with no motorized vehicles nearby (number16) have a low standard deviation. The different weather conditions and day times of our measurements play only a minor role for the standard deviation.

5.1.1.1 Evaluation of Street Parameters

5.1.1.1.1 Bike Path Categories

As can be seen in Table 8, the bike path categories show no distinguishable pattern. This might be due to the problem that small streets with no bike path show only little pollution, whereas highly frequented streets with no bike path show very high NO_2 concentrations. This is for example the case for Rohrbacher Straße (north part) (number 21) compared with Gaisbergstraße (number 22). Both Streets have no separated bike path, but only one is highly polluted.

5.1.1.1.2 Traffic Volume

We can compare the correlation between the different parameters and the NO_2 concentration in Table 8. Our own ranking of the traffic volume seems to well correlate with the NO_2 concentration. The streets marked with no traffic volume have the lowest NO_2 concentrations and the nine most polluted streets are ranked with a medium or high traffic volume.

5.1.1.1.3 Urban Canyons

Urban canyons need to be separated into canyons with higher traffic volume and canyons with lower traffic volume. The two street canyons with high traffic volume are the most polluted streets on our route. The street canyons with low traffic volume are not noticeably more polluted than other streets with low traffic volume.

5.1.1.1.4 Number of Lanes

Next, we can take a look at the effect of the number of lanes (excluding turnlanes) on the NO_2 concentration. Apart from the bridges over the Neckar we again have a clear correlation between NO_2 pollution and number of lanes. All five streets with four lanes (bridges excluded) belong to the eight dirtiest streets, whereas six out of eight streets with only one lane belong to the eight cleanest streets. However, as the number of street lanes correlated with the traffic volume, this result is not surprising. Unfortunately, this only holds true for our own counting of lanes. In data from OpenStreetMap, large streets tend to be separated into different objects. Then a large street contains numerous objects with only one or two lanes.

5.1.1.1.5 Street Type

Both rankings for the street types, our own as well as the one based on data from OpenStreetMap), correlate well with the NO_2 concentration. Note, that in Table 8 we assigned the same colour to the OSM categories “Track”, “Living street”, “Path” and “Residential”. Deviations from the correlation mostly occur for both rankings at the same time as for example in Bergheimer Straße or Berliner Straße. We can therefore assume that the reason for these deviations is due to circumstances that are independent from the category itself. This might be, for example, a very high air exchange rate due to a flat surrounding.

5.1.1.1.6 Speed Limit

On the contrary, the speed limit does not correlate very well with the NO_2 concentration. Most of the highly polluted streets have a high speed limit of 50km/h, but several streets that are low in pollutants have the same speed limit. Most times we only find two different speed limits inside the city – 30km/h and 50km/h. The number of different speed limits could be too low to allow a fine ranking.

5.1.1.1.7 Most Important Street Parameters

We can conclude that the volume of traffic followed by the street type is the most important parameter for predicting the NO_2 concentration of a road. In case a road has a high traffic volume and additionally is an urban canyon it can be predicted to have even higher NO_2 concentrations. In case a road is a bridge or has a very wide flat surrounding on either side and has a high traffic volume, the NO_2 concentration can be predicted to be lower than a normal street with high traffic volume.

Table 8 Correlation between different parameters and measured NO_2 concentration. For an improved overview we applied a colour scale to each column that ranged from green to red. Properties that most likely correlate with a low NO_2 concentration are coloured in green whereas properties that most likely correlated with a high NO_2 concentration are coloured in red.

Number	Street	Mean measured concentration $[\mu g/m^3]$	Annual mean (extrapolated) $[\mu g/m^3]$	Bike path categories[2] (own rating)	Cycleway category (OSM)	Traffic volume (own rating)	Urban canyon (according to character of surrounding, own rating)	Number of marked lanes on street (all directions)	Number of lanes (OSM, most times only one direction)	Street type (own rating)	Street type (OSM)	Speed limit (OSM)
2	Field path	12	11	3	-	None	No	1	1	Side	Track	-
9	Alte Brücke (old bridge)	18	16	3	-	None	No	1	1	Side	Living street	-
16	Bike path along old tracks	20	17	1	Designated	None	No	1	-	Side	Path	-
22	Gaisbergstraße	24	22	3	-	Low	Yes	1	1	Side	Residential	30
7	Theodor Heuss bridge	26	24	2	Use_sidepath	Medium	No	4	2	Main	Primary	50
24	Alte Bergheimer Straße	26	25	3	-	Low	Yes	1	-	Side	Residential	30
1	Berliner Straße	28	30	2	-	High	No	4	2	Main	Primary	50
26	Kirchstraße	28	51	3	-	Low	Yes	1	-	Side	Residential	30
5	Steubenstraße	29	33	2	Lane	Medium	North part due to big trees	2	2	Main	Primary	50

[2] Categories for the bike path: 1: bike path several tens of meters away from the car lane, 2: bike path next to car lane, 3: no bike path separated from the car lane

19	Karlsruher Straße	29	28	2/3	-	Low	Yes	2	-	Side	Secondary	20/50
20	Rohrbacher Straße (south)	29	29	2	Lane	Medium	No	2	-	Side	Primary	50
4	Rottmannstraße	30	34	2	Lane	Medium	Yes	2	2	Main	Primary	50
15	Rudolf-Diesel-Straße	30	26	3	-	Low	No	2	2	Side	Residential	50
25	Alte Eppelheimer Straße	30	26	3	-	Low	No	1	-	Side	Residential	30
17	Hebelstraße	32	31	3	Yes	Medium	No	2	2/1	Side	Secondary/tertiary	50
8	Neckarstaden	33	55	2	-	High	No	2	2	Main	Primary	50
10	Neuenheimer Landstraße	33	40	2	-	Medium	No	2	2	Side	Secondary	30
23	Poststraße	35	41	3	-	Low	No	1	-	Side	Residential	30
3	Dossenheimer Landstraße	36	48	3	-	High	By trend	2	2	Main	Primary	50
14	Speyerer Straße	36	44	2	No	High	No	4	2	Main	Primary	50
13	Lessingstraße	37	53	2	-	High	No	4	2	Main	Primary	50
27	Ernst Walz bridge	38	42	2	-	High	No	4	2	Main	Primary	50
11	Bergheimer Straße	40	45	3	-	Medium	Yes	2	1	Side	Tertiary	30
18	Römerstraße	40	41	2	-	High	No	4	2	Main	Primary	50
6	Brückenstraße	41	49	2	Lane	Medium	Yes	2	2	Main	primary	30
12	Mittermaierstraße	48	56	2	-	High	Yes	4	1	Main	Primary	50
21	Rohrbacher Straße (north)	49	64	3	Lane	High	Yes	2	-	Main	Primary	50

5.1.2 Comparison of Spatial Mean and Mean of Measurements

In chapter 4.3 we explained that the spatial mean is an instrument to calculate an average NO_2 concentration that weighs every part of the route the same. A crossing where we have measured for a longer period of time (because of the red traffic light) has the same weight as a part of the street we passed at a high speed and therefore have only few measured data points. Using the spatial mean we can evaluate the route independently of the number of measurements that we have for certain parts of the route. On the other hand, to calculate a realistic NO_2 concentration a cyclist is exposed to on the route, measurements taken at a crossing (where the cyclist spends more time than on a straight part of the street) more. For this purpose, it is more adequate to just use the mean of all of our route measurements, because we ourselves were cycling along the road and had to spend more time on a crossing with a red traffic light. The question is, how much both mean values – the global spatial mean and the total mean of all of our measurements – differ. Surprisingly, for the spatial mean values presented in Table 4 the exact total mean of our measurements differ by less than 2%. Therefore, the results in Table 4 are the same for the mean value (instead of the global spatial mean) of all respective measurements. This, of course, is only the case for our measurement data. In general, for a set of measurements, the differences between the spatial mean and the total mean of the measurements themselves can differ significantly. Especially for a small set of measurements, the spatial mean does not consider a relatively high number of data points (see the description of the threshold for a minimum of data points within a square before the mean value becomes considered in chapter 4.3) For other measurements this could be different, and therefore it is good to keep the global spatial mean as an instrument to assess a measurement route under certain conditions. However, the spatial mean is not suited for only a few measurement runs, as in this case most of the measurement data is not considered for the global spatial mean.

5.2. Point Measurements

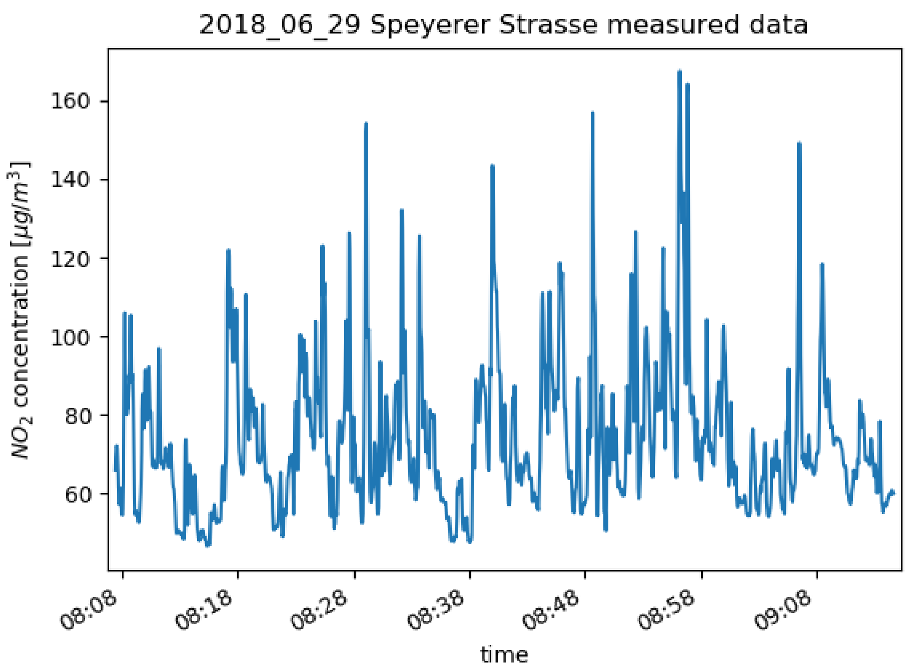

Figure 23 Measured NO2 concentration at Speyerer Straße in the morning of 29th June. Note that the y-axis values start at $40\mu g/m^3$.

In the following chapter we will present the results from our point measurements that were executed at the locations marked in Figure 9. Figure 23 shows the measured NO_2 concentration on a Friday morning at Speyerer Straße. As we can see, the concentration varies within several seconds. Every couple of minutes the variation is in the order of up to $100\mu g/m^3$. This is due to the traffic light cycle but also due to the types of vehicles that pass the measurement instrument on the street. Especially trucks that passed on the side of the road where the instrument was situated, caused exceptionally high peaks. The measurement instrument was not situated directly at the traffic light, but the traffic was still accelerating when passing the instrument. Also, most likely the local wind turbulences had a strong influence on the measured concentration. Even if the general wind speed and direction several meters above the ground is stable, buildings, the traffic and other wind barriers cause a fluctuation in wind speed and direction around the measurement instrument. So periods of several minutes, where the concentration of NO_2 seems to be low, could be caused by the fresh air coming from the direction opposite to the street. It is important to note that in Figure 23 the y-axis values start at $40\mu g/m^3$. Therefore, over the whole time the measured NO_2 concentration was very high. It was the point measurement with the highest mean NO_2 concentration. In contrast, Figure 24 presents one of our point measurements at Speyerer Straße with the lowest concentrations from all of our point measurements.

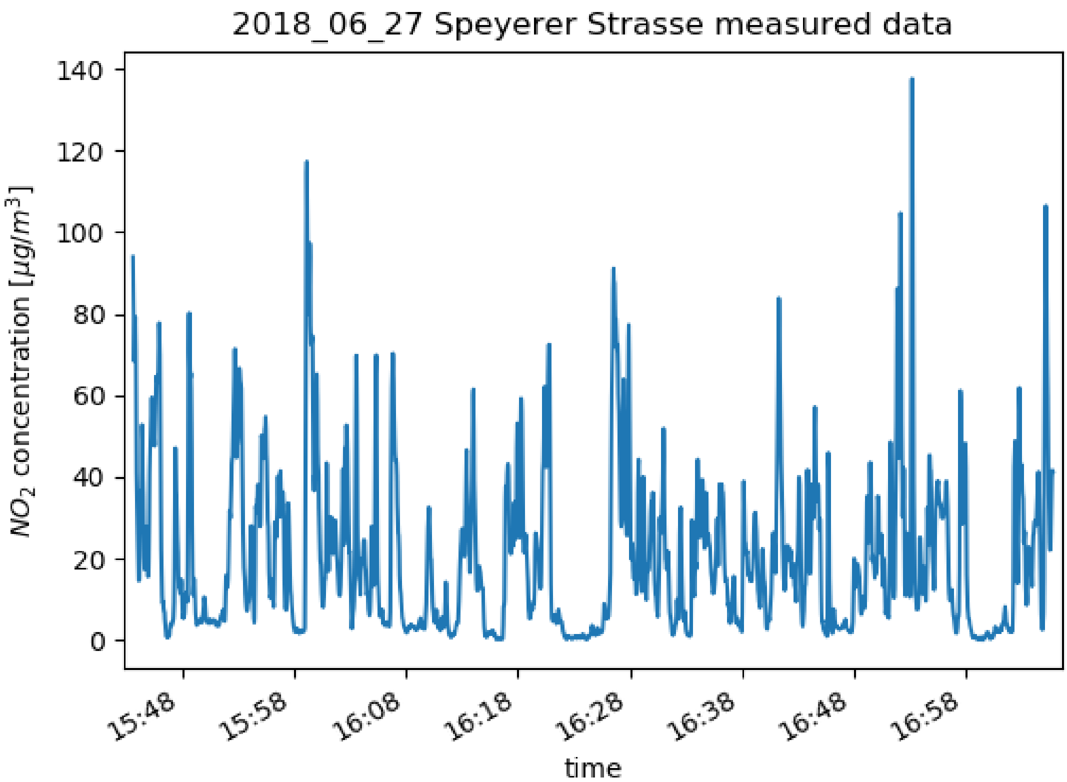

Figure 24 Measured NO2 concentration at Speyerer Straße on Wednesday evening on 27nd June

The other point measurements show the same characteristics. Each time the plot shows a constant or very slowly changing background NO_2 concentration and above that many brief peaks. These peaks can be very high, depending on the kind of vehicle that passed the instrument. At the same time these peaks never last longer than about one or two minutes. After this period of time, the air masses seem to have mixed. An overview of the resulting mean NO_2 concentrations for the point measurement runs is given for each site in Figure 25.

As you can see in Table 15 and Table 16 in the appendix, we have tried to execute the point measurements at each site at different times of the day. We are interested to know how the NO_2 concentration changes according to day time. Usually one would expect two peaks during a day, due to the commuter traffic: One in the morning and one in the late afternoon. However, our results look different. There are many point measurements with high mean values that were executed during typical off peak times as was the case for Brückenstraße on Friday 29th June from 10:43 to 11:43 or for Neckarstaden on Wednesday 27th June from 14:16 to 15:18. Due to the high volume of traffic a cyclist can be exposed to very high NO_2 concentrations throughout the whole day. Regarding the measured mean NO_2 concentrations in Table 15 we find that for each measurement site the average of all measurement runs is below the annual threshold of $40\mu g/m^3$. However, the averages in case of Brückenstraße, Neckarstaden and Speyerer Straße are below the threshold by $2\mu g/m^3$ or $3\mu g/m^3$ only. Also, the one hour mean of single point measurement runs exceeds the threshold value for each site one or two times.

It is most likely that during daytime for each site an hourly mean of $40\mu g/m^3$ on average is exceeded. We can assume this because all point measurements were executed during daytime in summer. However, as we saw in Figure 20, the measurement runs in winter time showed higher NO_2 concentrations than in summer time. This assumption is also supported by the average of the extrapolated annual mean values based on all point measurements for each measurement site in Table 16.

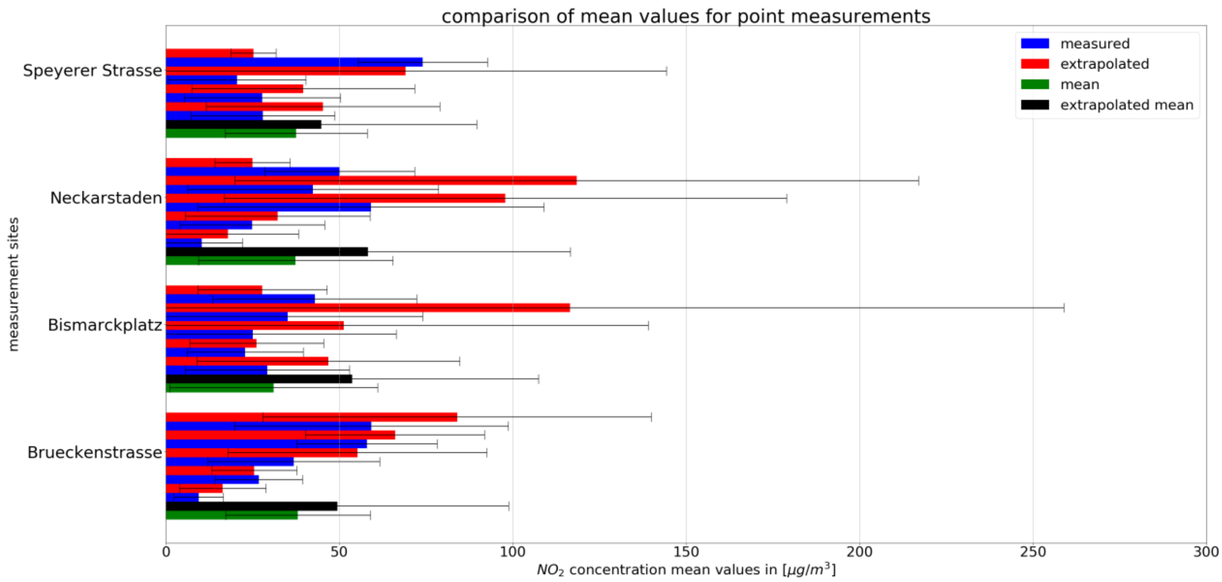

Figure 25 Comparison of mean NO_2 concentrations and extrapolated annual mean concentrations for each point measurement inn blue and red. In green and black the overall mean values for all measurement data for each measurement point are represented. The error bars do not represent the error but the standard deviation of each measurement.

To conclude, we can say that the measurement sites that we chose really turned out to be highly polluted roads in Heidelberg. The results suggest that the surrounding of the road as for example high buildings or a huge water surface only have a minor effect on the NO_2 exposure to cyclists. Far more important is the traffic volume – which was very high at all sites that we picked.

5.3. Extrapolated Rush Hour NO2 Concentrations

In chapter 4.1 we have analysed the mean NO_2 concentrations for different conditions and calculated the coefficients to calculate the extrapolated mean concentration from the extrapolated annual mean. Here we want to make use of it. We will try to predict how a cyclist, who rides his bike to work on a workday between 8:00 and 9:00 (CET) during school time, will be exposed to NO_2. The coefficient to convert the extrapolated annual mean into an extrapolated mean value for this typical journey to work is 1.5 according to Table 17 in the appendix. This leads to an extrapolated NO_2 concentration of $60\mu g/m^3$ on average for the whole route. Compared to the annual threshold for NO_2 this is still very high. Also, this extrapolated mean value turns out to be higher than the mean NO_2 concentration of all peak measurements that were executed without breaks. In chapter 5.1.4, we found a mean value of $40\mu g/m^3$ for all peak measurements that were executed.

For the individual streets we have calculated the resulting extrapolated NO_2 concentrations during the morning commuter traffic presented in Table 9. The colours visualize the mean values on a scale of $11\mu g/m^3$ (green) to $96\mu g/m^3$ (red). While for the extrapolated annual mean 12 streets exceeded $40\mu g/m^3$, during the morning commuter traffic, when a lot of cyclists are on the way to work, 19 streets even have concentrations above $40\mu g/m^3$. According to the EU regulations this would not be against the law, as the hourly threshold of $200\mu g/m^3$ is not exceeded.

Table 9 Extrapolated annual mean NO_2 concentration compared to extrapolated mean NO_2 concentration in commuter traffic for streets of route. Concentrations above $40\mu g/m^3$ are highlighted. The colour scale ranges from $11\mu g/m^3$ (green) to $96\mu g/m^3$ (red). Concentrations over $40\mu g/m^3$ are highlighted. The street to the corresponding number can be found on the map in Figure 8.

Street number	Street	Measured mean $[\mu g/m^3]$	Annual mean (extrapolated) $[\mu g/m^3]$	Commuter traffic mean (extrapolated) $[\mu g/m^3]$
1	Berliner Straße	28	30	***45***
2	Field path	12	11	16.5
3	Dossenheimer Landstraße	36	***48***	***72***
4	Rottmannstraße	30	34	***51***
5	Steubenstraße	29	33	***49.5***
6	Brückenstraße	***41***	***49***	***73.5***
7	Theodor Heuss bridge	26	24	36
8	Neckarstaden	33	***55***	***82.5***
9	Alte Brücke (old bridge)	18	16	24

10	Neuenheimer Landstraße	33	40	***60***
11	Bergheimer Straße	40	***45***	***67.5***
12	Mittermaierstraße	***48***	***56***	***84***
13	Lessingstraße	37	***53***	***79.5***
14	Speyerer Straße	36	***44***	***66***
15	Rudolf-Diesel-Straße	30	26	39
16	Bike path along old tracks	20	17	25.5
17	Hebelstraße	32	31	***46.5***
18	Römerstraße	40	***41***	***61.5***
19	Karlsruher Straße	29	28	***42***
20	Rohrbacher Straße (south)	29	29	***43.5***
21	Rohrbacher Straße (north)	***49***	***64***	***96***
22	Gaisbergstraße	24	22	33
23	Poststraße	35	***41***	***61.5***
24	Alte Bergheimer Straße	26	25	37.5
25	Alte Eppelheimer Straße	30	26	39
26	Kirchstraße	28	***51***	***76.5***
27	Ernst Walz bridge	38	***42***	***63***

We can do the same kind of analysis for the point measurements. As the extrapolated annual mean already exceeded the annual threshold at all measurement sites, the extrapolated concentration on a morning of a workday during school time is exceptionally high at all measurement sites.

Table 10 Extrapolated annual mean NO2 concentration compared to extrapolated mean NO2 concentration in commuter traffic at point measurements. Concentrations above $40\mu g/m^3$ are highlighted.

	Measured $\mu g/m^3$	Annual mean (extrapolated) $\mu g/m^3$	Commuter traffic mean (extrapolated) $\mu g/m^3$
Brückenstraße	38	***<u>49</u>***	***<u>73.5</u>***
Bismarckplatz	31	***<u>54</u>***	***<u>81</u>***
Neckarstaden/B37 near Marstall	37	***<u>58</u>***	***<u>87</u>***
Speyerer Straße	38	***<u>45</u>***	***<u>67.5</u>***

6. Improvement of Extrapolation

In the previous chapters (e.g. 5.1.2, 5.2 and 5.3) we extrapolated our measurement data to an annual mean for different applications. As we could see, the resulting data was not always satisfying: Depending on the data we used for the extrapolation, the extrapolated annual mean fluctuates very strongly even though the extrapolation was meant to eliminate the fluctuations in our measurements. For example the extrapolated annual mean based on our winter measurements deviated from the one based on the summer measurements by 54% in Table 4 in chapter 5.1.3. For the point measurements, the extrapolated annual mean (based on single one hour lasting measurement runs in Table 16 in the appendix) variated for Brückenstraße between $16\mu g/m^3$ and $84\mu g/m^3$ which is equivalent to a deviation by 525%. In this chapter we will discuss the reasons why this extrapolation did not work as well as it was expected, and we will discuss different approaches to improve the extrapolation method.

6.1 Differences in Variation of NO_2 Concentrations between Measurement Site Compared to the Measurement Station

Firstly, we would like to have a look at the low extrapolated annual mean from the winter data and the high extrapolated annual mean from summer data from the bicycle measurements in chapter 5.1.3. For the extrapolation we used the data from the one existing LUBW station in the north of the city (see Figure 8). We seem to overestimate the annual mean concentration if we measure at times when the NO_2 concentration is relatively low (summer) and underestimate the annual mean, when we measure at times with relatively high NO_2 concentrations (winter). The effect is so strong, that in winter time the extrapolated annual mean concentration is lower than the actual mean values measured in summer and vice versa. To find the reason for this behaviour, we have a look at our extrapolation formula from equation (30). On the one hand, to overestimate the annual mean NO_2 concentration at the local measurement point when the local measurement takes place at a time where the measurement station measures a lower concentration than the annual mean of the station, the coefficient c_{ams}/c_s must be too high. On the other hand, to underestimate the annual mean concentration at times with a higher NO_2 concentration at the measurement station than in the annual mean (for example during an inversion), the coefficient c_{ams}/c_s must be too small. The coefficient seems to adopt rather extreme values. This leads to the conclusion that most likely the actual variation of the measured NO_2 concentration at the station depending on the time of the day and the weather conditions is higher than the variations of our bike measurements. In other words, there must be a seasonal variation in the NO_2 concentration at the station (e.g. because in winter time we have more days with inversion than in summer) that is weaker for our local measurements. If we consider the field path (number 2 in Figure 8) of our route (Figure 8) this might be true, as even during an inversion the air is less polluted outside the city on the fields than in the city centre. This means that the NO_2 concentration is rather constant on this path as even during an inversion the NO_2 does not distribute from the city to the fields nearby (depending on the wind direction). However, for all streets in the city the effect of the inversion should be more or less the same (that means the NO_2 concentration should vary just as much as it does at the station) and our method to extrapolate the annual mean concentrations should deliver the same approximate annual mean, no matter whether we measure during an inversion or not.

Another explanation could be that the distance from the air sampler to the traffic plays a role. While the measurement station is situated several meters away from the street lane, we measure the NO_2 concentration right on the street. Therefore at the station the pollutants have more time to distribute homogeneously in the air before the measurement station measures the concentration than in the case of our measurement system. The station would then measure the background in the city to a larger extend than we do. Hence the station data would depend on the weather to a greater extend while for the bike measurements the actual traffic volume is important to a greater extend. If this was true, our measured concentrations would be rather independent of the weather and should give the same average concentrations in summer as in winter time. A look in Table 4 reminds us that this is obviously not the case and can thus not on its own explain the extrapolation difference.

6.2 Accounting for NO_2 Background

We could think of a background NO_2 concentration that changes over the year. It was our assumption that for all local places the measurements deviate from the local annual mean by the same factor of proportionality as the hourly mean at the measurement station differs from the annual mean measured by the measurement station. However, in case there is an offset of the NO_2 concentration of the same absolute value all over Heidelberg, a variation in this offset would not be compatible with the proportionality as long as the measurement station and the local point do not have the same annual mean. Remembering chapter 4.2 we find that the background NO_2 concentration actually does changes over the year. We therefore improve our extrapolation method. We will subtract the background NO_2 pollution before the extrapolation and add it again afterwards. This way we only correct the NO_2 pollution caused by emitters in the city. The resulting extrapolation formula then becomes:

$$\mathrm{c_{aml}} = \mathrm{c_{am,back}} + (\mathrm{c_l} - \mathrm{c_{back}}) \frac{\mathrm{c_{ams}} - \mathrm{c_{am,back}}}{\mathrm{c_s} - \mathrm{c_{back}}} \tag{32}$$

With “am” for annual mean, “back” for background concentration, “s” for station and “l” for local. Due to the far distance of more than 100 km to the nearest background measurement station, the background for Heidelberg and for the station at the Schwäbische Alb (see chapter 4.2) do not correlate for each hour. We therefore use the monthly mean of the station at the Schwäbische Alb instead of the hourly mean of the station for c_{back}. We test this method and calculate the extrapolated annual mean using the measurement data from all measurement runs, separated into summer and winter data. This time we get even worse results: The extrapolated annual mean from the winter data is now $22\mu g/m^3$ (formerly $28\mu g/m^3$) and $195088396128\mu g/m^3$ (formerly $42\mu g/m^3$) for the annual mean extrapolated from the summer data. Obviously this approach did not solve our problem as we can see on the arbitrary huge NO_2 concentration (no, this is no typing mistake as we will explain in the next sentences). If we subtract the background, the variation of the extrapolated annual mean seems to be even higher for the measurement station than for our own measurements – and absolutely unreasonable. To analyse this effect for differently high background concentrations, in Table 11 we multiplied the background concentration by several scaling factors and then again calculated the extrapolated annual mean based on the measurement data for both seasons using (32). For none of the scaling factors the extrapolated annual mean from the summer data assimilates to the extrapolated annual mean from the winter data. However, for a scaling factor of two we even get minus infinity. But how can that be? The problem is that it can happen that c_s and c_{back} have (almost) the same value. Then we divide by (almost) zero and (32) cannot be valid anymore. Also negative concentrations may possibly occur if the NO_2 concentration at the station is lower than the mean background concentration. This leads to the conclusion that this attempt fails in case the measured concentration at the station is of about the same as the background NO_2 concentration. As we had no access to hourly mean NO_2 background concentrations nearby but had to use mean values from the Station at the Schwäbische Alb (see chapter 4.2) this can easily occur under certain weather conditions with low NO_2 concentrations at the measurement station in Heidelberg.

Table 11 Mean extrapolated annual NO_2 concentration for winter and summer runs depending on a scaling factor of the background NO_2 pollution. Note that here we do not use the global spatial mean. In case the background concentration is just about the hourly mean of the measurement station in Heidelberg the extrapolated mean becomes arbitrary large due to a division of a number close to zero.

Scaling factor of background	Mean of extrapolated winter data	Mean of extrapolated summer data
0	28	42
0.5	28	45
0.8	26	52
1	22	195088396128
1.3	28	68
1.5	30	80
2	44	-infinity

6.3 Mean Extrapolation Coefficient

Another aspect regarding the quality of our extrapolation method is the variation of the difference between the measured and the extrapolated values for the different streets in Figure 22. Generally, the reason for this phenomenon must be different extrapolation factors for different streets. This would mean that we measured the different streets at different times, because during several minutes the extrapolation factor does not change that much. But we note that also streets that follow each other on the route and are therefore measured only several minutes after each other show these differences. So the reason must be something else. Possibly it is caused by the mixture of measurement runs of different days. Assume on one day we catch the plume of a bus in one street and the extrapolation factor for this day is very high and on another day we catch it in the other street, but the extrapolation factor is very low. Then the resulting mean values that we measure are high in both cases. But the extrapolated values are only exceptionally high in one case. To solve this problem, we will average the extrapolation coefficients from all considered measurement runs and apply the same (averaged) extrapolation coefficient to all considered measurements instead of the individual extrapolation coefficients. This way, the deviation for all streets must become equal. To have a look at the quality of this method to gain the extrapolated annual mean, we use the point measurement data and perform the new extrapolation method. The results are shown in Table 12. For three out of four measurement sites the results are more or less the same as in our old method. However, in the case of Speyerer Straße, the new extrapolation method gives completely different values. Searching for the reason, we find one measurement at Speyerer Straße with very high NO_2 concentrations that was performed during the event of an inversion. All the other measurements were executed during normal NO_2 pollution at the measurement station at Berliner Straße. As a result the normal extrapolation method lowered the high NO_2 concentrations from the last measurement (as also at Berliner Straße there were very high NO_2 concentrations, far above the annual mean). On the contrary, the new extrapolation method only corrected the high values at Speyerer Straße by the mean of the coefficients of the considered single measurements. As all the other measurements took place under usual conditions, this mean factor was not sufficient to lower the measurement values during the inversion. As a result the extrapolated annual mean from the new method was much higher (example with concrete arbitrary numbers: $(2 \cdot 5 + 6 \cdot 0.5)/2 = 6.5$ but $2 \cdot 2.7 + 6 \cdot 2.7)/2 = 10.8$). We therefore conclude that this attempt to improve the extrapolation method also did not help to improve our extrapolation.

Table 12 Comparison of extrapolation method with single extrapolation coefficient for each measurement to extrapolation with averaged extrapolation factor for all measurements. The two mean values that deviate most are highlighted.

Site	Annual mean (extrapolated, single coefficient for each measurement)	Annual mean (extrapolated, mean extrapolation coefficient)
Brückenstraße	49	55
Bismarckplatz	54	55
Neckarstaden/B37 near Marstall	58	61
Speyerer Straße	***45***	***67***

Unfortunately, this means that all attempts to improve the extrapolation method have not succeeded. It seems that the variation of the NO_2 pollution at our measurement sites is too different and uncorrelated to the one at the measurement station at Berliner Straße, resulting in a large error in the extrapolation of measurements to annual mean values. Reasons for this might be the different traffic volumes but also measurements in the plume of vehicles that cause exceptionally high values that do not correlate with the station. Another reason could be the position of the measurement station as discussed in the next chapter 6.4

6.4 Position of Measurement Station

As we found in chapter 5.1.3 the extrapolation of our measurement data using the one hour mean values from the measurement station at Berliner Straße leads to too high or too low extrapolated annual mean values, depending on the season we recorded the measurement data used for the extrapolation. This can lead to the suspicion that the measurement station is situated at a position in Heidelberg that is often less polluted than highly frequented streets in the city centre, as for example the north part of Rohrbacher Straße (street number 21 in Figure 8). But for our extrapolation we need hourly mean data from a station that actually measures all the rush hour peaks in pollution and not just a background. Unfortunately there is no further measurement station in Heidelberg available that measures hourly mean concentrations. The next measurement station that is exposed to the NO_2 pollution in a larger extent can be found in Mannheim (about 16 km air distance from Heidelberg). In a first approach we extrapolated our measurement data once more, using the hourly mean values from the measurement station at Mannheim Friedrichsring. The results need to be analysed in greater detail in the future. However, the first results in Figure 26, Figure 27 and Figure 28 look quite different in the extrapolated annual mean values compared to Figure 20, Figure 22 and Figure 25. The only difference in the extrapolation procedure was that we used hourly mean values from a different measurement station. The two major observations are that the mean measured concentrations and the extrapolated annual mean concentrations are very similar for the measurement runs in Figure 26 and Figure 27. For Figure 28 they still differ, but much less than they did originally in Figure 25. This suggests that our bicycle measurements already give a representative annual mean NO_2 concentration. On the other hand, in Figure 26 the extrapolated annual mean based on our winter measurements ($39\mu g/m^3$) deviates from the extrapolated annual mean based on our summer measurements ($32\mu g/m^3$) by 22%. Therefore, using hourly mean values from the measurement station in Mannheim seems to improve our extrapolated annual mean values but is still not a perfect solution.

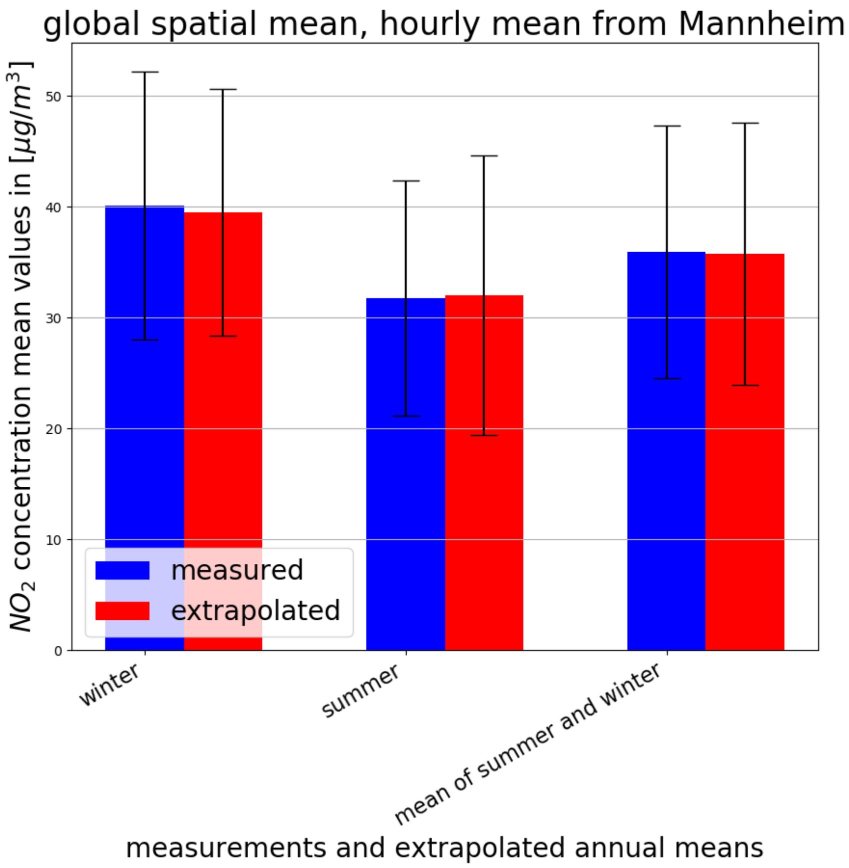

Figure 26 Comparison of mean from measurement data (except point measurements) to mean of extrapolated annual mean. The comparison is done for all data as well as for data collected in winter and summer time separately. The error bars represent the standard deviation of the measurement data and not the uncertainty of our measurements. Peak and off-peak measurements are not distinguished here. The red bars for winter and summer represent the extrapolated

annual mean based on the measurement data of only the respective season. For the extrapolation we used hourly mean values from the measurement station in Mannheim at the Friedrichsring.

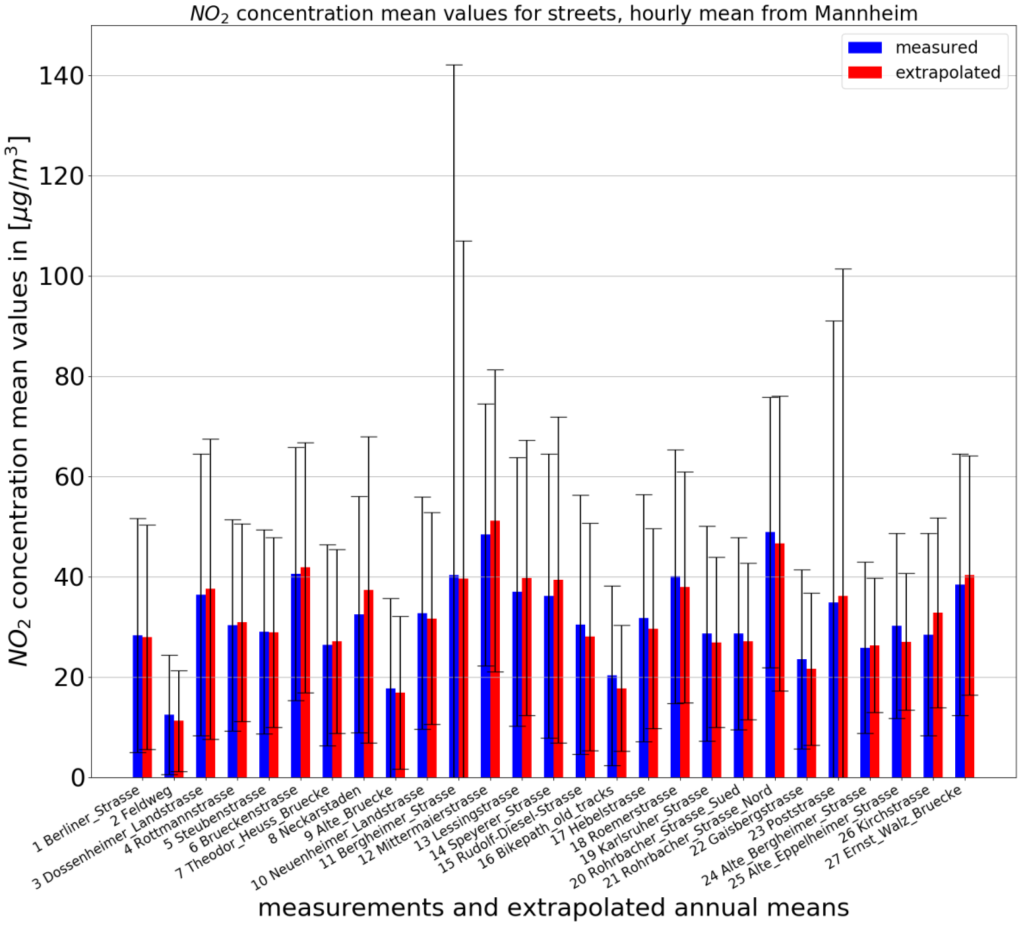

Figure 27 Mean NO2 concentrations for all streets. Mean values for measured data in blue and extrapolated data in red. The error bars represent the standard deviation (and not the error) of the data points for each street. For the extrapolation we used hourly mean values from the measurement station in Mannheim at the Friedrichsring.

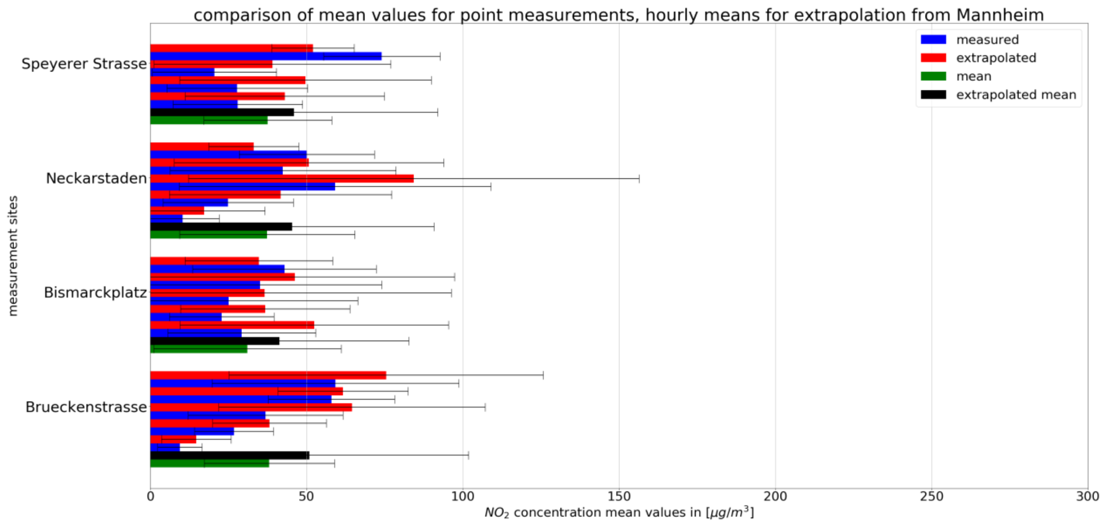

Figure 28 Comparison of mean NO_2 concentrations and extrapolated annual mean concentrations for each point measurement inn blue and red. In green and black the overall mean values for all measurement data for each measurement point are represented. The error bars do not represent the error but the standard deviation of each measurement. For the extrapolation we used hourly mean values from the measurement station in Mannheim at the Friedrichsring.

7. Discussion

7.1 Assessment of the NO_2 Pollution in Heidelberg

The mean NO_2 concentration of our summer and winter measurement runs is $36\mu g/m^3$ (as we executed more summer measurements than winter measurements this does not correspond to the mean of all our bicycle measurements) and therefore $4\mu g/m^3$ below the annual average threshold of $40\mu g/m^3$ according to Table 4. A comparison of the bicycle measurements between different seasons shows a significant variation over the year in chapter 5.1.3. While the mean NO_2 concentration of our summer measurements is $32\mu g/m^3$ it is $40\mu g/m^3$ for the winter measurements. Even a larger difference is shown in Table 5 for the peak time measurements. While for wintertime the NO_2 concentration is about $52\mu g/m^3$ for summer time it is $37\mu g/m^3$. On the contrary, the off-peak measurements show a similar concentration for both seasons ($17\mu g/m^3$ in winter time and $14\mu g/m^3$ in summer time). Considering the average of all measurements, according to Table 8 only in three streets a mean measured concentration of $40\mu g/m^3$ is exceeded. At the four point measurement sites the measured mean NO_2 concentration is below $40\mu g/m^3$. However, the mean concentrations for single one hour lasting point measurements could be very high – sometimes up to $74\mu g/m^3$ (see Table 15). Concentrations above $40\mu g/m^3$ seem to occur at all point measurement locations during rush hours on a regular basis. Even though the one hour mean does not exceed the short time exposure threshold of $200\mu g/m^3$, we strongly recommend everyone to avoid areas with a large traffic volume on his or her way to work. This remains true also for well ventilated places and streets with a high volume of traffic, since, depending on the wind direction, one may be directly in the plume of the vehicles (compare hourly mean values in Table 15 for Neckarstaden/B37 close to the river bank).

Although the extrapolated annual mean values fluctuated depending on the measurement data we used for the extrapolation, also the extrapolated annual mean values suggest NO_2 concentrations well above the annual mean threshold of $40\mu g/m^3$ in several streets with high traffic volume (compare results in Table 8).

To protect cyclist from highly polluted streets on their bike rides, it would be desirable to offer navigating systems that can consider the NO_2 pollution when calculating a route. In order to do so, needs to access parameters that indicate the NO_2 concentration most likely found in a street. In Table 8 we found that the self-assessed traffic volume and the street type categories from OpenStreetMap correlate well with the NO_2 concentrations we measured in the streets. Therefore these parameters might be used for a routing algorithm that considers the NO_2 pollution a cyclist is exposed to. Additionally he could consider the differences in NO_2 pollution between rush hours and off-peak times during for example Sundays that were found in 5.1.4.

7.2 Quality of Extrapolated Mean Values

In this thesis we had a close look on the extrapolation of measurement data and the variations of NO_2 pollution at the measurement station. It was our aim to find a way how to best predict the mean NO_2 concentration for certain times. Unfortunately, the extrapolated mean values are not always reliable due to the following observations. Firstly, extrapolated annual mean values from summer data and from winter data did not agree with each other very well. They deviated by 54%. Secondly, the difference between the measured and the extrapolated mean value varies largely between different streets. Thirdly, the point measurements in Figure 25 show a very high fluctuation of the extrapolated annual mean values for each site for different point measurements at different times. For our point measurements, the extrapolated annual mean fluctuates by up to $100\mu g/m^3$. As each measurement run lasted for about an hour, this effect was most likely not caused by statistical fluctuations of the traffic that passed the measurement instrument. This is a hint that our extrapolated annual mean values for the streets still depend on the actual times, weather conditions and traffic volume for our single measurements. It seems as though the diurnal variations of the NO_2 concentration at our measurement sites do not correlate with the measurement station to an extent that justifies our assumption of proportionality for our extrapolation. The reason for this behaviour could be different diurnal variation of the traffic volume, different effects of the wind direction and speed due to different surroundings and maybe partly a different composition of the vehicles in the traffic. However, above all the position of the measurement station that is *not* at a position with very high traffic and bad air circulation (see Figure 8) opposes the assumption of proportionality.

7.3 Measurement Stations

While for the measurement station at Berliner Straße (Number 1 in Figure 8) our measured and extrapolated annual mean NO_2 concentrations agreed with the annual mean measured by the measurement station within a maximum deviation of 19%, the bicycle measurements at Mittermaierstraße did not agree with the annual mean value from the passive sampler. There are several circumstances that may have caused these variations.

Since we measured very high concentrations on the bike lane just next to the cars, there might be a high gradient of the NO_2 concentration in the surroundings. This means that the background NO_2 concentration a little further away (e.g. behind the next block of buildings) is likely to be much lower and the NO_2 concentration one measures probably drops very fast when moving away from the street. The airsampler of the measurement station is fixed to a road sign approximately three to four meters above the ground. Moreover, it is situated on the opposite side of the street as compared to where we measured on the bike path. These circumstances might partly explain the variation, but it is questionable whether these findigs are sufficient to explain the deviations completely. Another point is that the coefficients for our extrapolation are taken from the measurement station at Berliner Straße. Therefore we could expect that the extrapolation is not as precise for Mittermaierstraße as it was for Berliner Straße. Above all, the LUBW does not publish the errors of their measurement data. While our ICAD measurement instrument can be assumed to have only an error of few percent, the chemiluminescence detektors (used mostlikely in the measurement station from the LUBW) are reported to have errors of several tens of percent. [11] The error of the passive sampler used at Mittermaier straße is also unknown to us.

7.4 Outlook

In order to predict the annual mean concentrations of NO_2 from only few measurements on a measurement site, more research has to be done. It might be interesting to conduct further point measurements in certain distances from the station at Berliner Straße and at Mittermaier Straße. This way one could try to assess how long one actually needs to measure at a certain point to get reliable mean values. Also, further data analysis could be performed to find out more about the role of certain weather conditions on the NO_2 concentration. These results might then be used for an improved extrapolation method and help to figure out whether an executed measurement was done at conditions with a lower or with a higher NO_2 pollution compared to the annual average. Also, one could try to improve the extrapolation method by using hourly background mean values instead of monthly averages. A precondition for this would be to conduct measurements in the close surrounding of a measurement station for the background NO_2 concentration. Another approach would be to investigate the role of high peaks in the measurement data. Maybe one can find an improved extrapolation method that splits the measured NO_2 concentrations (from a point measurement) into a continuous part and the highly fluctuating peaks. Finally, the role of the measurement station in Mannheim Friedrichsring compared to the measurement station in Heidelberg at Berliner Straße for the extrapolated annual mean values should be further analysed. The first results in chapter 6.4 give the impression that this might be the most successful approach in order to improve the extrapolated annual mean concentrations.

8. List of Figures and Tables

8.1. List of Tables

8.2. List of Figures

9. References

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- Maybritt Schillinger, Jan Baumgärtner, Adelheid Fischer and many others for cross checking my thesis for any kind of mistake.

11. Declaration of Honesty

I hereby declare that the submitted thesis is my own work and I did not use any but the acknowledged sources and aids.

Ich versichere, dass ich diese Arbeit selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

________________________________ ________________________________

Ort, Datum Unterschrift

12. Appendix

Table 13 Overview over all measurement runs. In the description of the route the numbers of the streets according to Figure 8 are given. "-" means the next street was directly measured, "to" means all streets with numbers in-between have been measured and "," means that the measurements were intermittent.

Run	Date and time	Weather (Temperature, wind speed, wind direction and precipitation)	Description of the route	Exceptional occurrences
1*	Tu 28.11.17 16:43-19:36	5.4°C, 2.6m/s from south and no rain	1-27-12 to 22	
2*	Tu 05.12.17 07:33-10:01	3.3°C, 2.1m/s from southwest and no rain	1-27-12 to 22	
3*	Tu 05.12.17 14:54-16:59	5.6°C, 2.7m/s from southwest and no rain	27-1 to 8-11-23 to 26	
4*	We 06.12.17 07:34-09:58	3.6°C, 2.2m/s from south and no rain	1-27-12 to 22	
5*	Th 07.12.17 15:20-17:26	7.1°C, 4.0m/s from south and no rain	Whole route except south of 1	
6*	Fr 08.12.17 07:30-09:26	5.1°C, 2.2m/s from west and no rain	Whole route	
7*	Su 10.12.17 08:11-10:02	0.3°C, 5.3m/s from east and no rain	Whole route	Off-peak
8*	Su 10.12.17 15:04-16:58	2.5°C, 5.5m/s from south and no rain	Whole route	Off-peak
9	Th 26.04.18 07:19-10:36	11.1°C, 4.1m/s from west and no rain	North of 1-3 to 7-part of 11	
10	Fr 27.04.18 07:01-09:42	10.5°C, 1.9m/s from east and no rain	Whole route except south of 1	
11	Fr 27.04.18 17:01-19:16	22.1°C, 3.2m/s from southeast and no rain	Whole route + 18 twice	
12	Su 29.04.18 14:57-17:29	27.2°C, 4.3m/s from east and no rain	Whole route	Off-peak
13	Mo 30.04.18 7:13-09:08	12.6°C, 3.7m/s from south and no rain	Whole route	
14	Mo 30.04.18 15:48-18:08	18.2°C, 6.9m/s from southwest and no rain	Whole route except 8 to 11,23 to 26	
15	We 02.05.18 7:11-09:25	8.4°C, 1.0m/s from southwest and no rain	Whole route	
16	Th 03.05.18 7:10-09:24	12.3°C, 1.5m/s from north and no rain	Whole route	Inversion

17	Th 03.05.18 15:00-17:13	24.5°C, 3.4m/s from north and no rain	2,3 to 5,9,12 to 16,19	
18	Fr 04.05.18 08:02-09:50	15.4°C, 1.3m/s from north and no rain	Whole route	
19	Fr 04.05.18 15:30-18:07	26.7°C, 4.4m/s from northeast and no rain	Whole route	
20	Fr 22.06.18 13:18-14:04 15:15-15:23 16:23-16:34 17:37-17:59 18:59-19:20	20.0°C, 5.2m/s from northwest and no rain	1 to 6, 13, 8, 8-11 to 14, 14-13-12-27-1	
21	Mo 25.06.18 06:56-08:55	16.4°C, 1.7m/s from northwest and no rain	Whole route	
22	Mo 25.06.18 08:57-09:19 10:19-10:24 11:24-11:34 12:36-13:08 14:10-14:25	22.4°C, 2.5m/s from northwest and no rain	1 to 6, 13, 8, 8-11 to 14, 14-13-12-27-1	
23	Tu 26.06.18 15:57-17:40	26.5°C, 2.1m/s from northeast and no rain	Whole route	
24	We 27.06.18 11:27-12:01 13:02-13:07 14:07-14:16 15:18-15:45 17:07-18:06	29.3°C, 3.2m/s from northeast and no rain	once whole route: 1 to 6, 13, 8, 8 to 14, 14 to 21	Around 16:00: soccer game for world cup with German team
25	Fr 29.06.18 07:06-08:10 09:16-10:10	20.8°C, 1.2m/s from southwest and no rain	Once whole route: 1 to 14, 14 to 27	Inversion
26	Fr 29.06.18 10:16-10:43 11:43-11:49 12:53-13:02 14:04-15:32	29.9°C, 2.6m/s from east and no rain	Once whole route: 1 to 6, 7, 8, 8 to 14, 14 to 27	Inversion from early morning ended
27	Fr 29.06.18 15:32-15:54 17:02-17:12	33.7°C, 1.9m/s from north and no rain	1 to 6, 6-5-4-3-2-1	
28	Tu 03.07.18 07:33-08:05 09:05-09:21 10:21-10:34	24.1°C, 1.0m/s from north and no rain	1-27-11-8, 8-11, 11-27-1	
29	Fr 06.07.18 07:17-09:11	20.8°C, 1.0m/s from northwest	Whole route	

		and no rain		
30	Fr 06.07.18 15:20-17:34	26.4°C, 3.9m/s from east and rain	Once whole route +27-1 twice	Heavy shower
31	Mo 09.07.18 07:12-08:57	19.8°C, 1.0m/s from north and no rain	Whole route	
32	Mo 09.07.18 08:59-10:49	25.2°C, 3.9m/s from northwest and no rain	Whole route	
33	Fr 27.07.18 12:08-14:33	34.6°C, 3.8m/s from east and no rain	1 to 11-21-22-27-1	During second day of school holiday
34	Su 29.07.18 11:39-13:25	28.8°C, 3.6m/s from southeast and no rain	Whole route	Off-peak, Neuenheimer Landstraße closed due to public event, street works at Main station
35	Su 29.07.18 11:25-13:04	28.3°C, 3.6m/s from south and no rain	Whole route	Off-peak, Street works at Main station

The measurements marked with a '' were executed in winter time by Richard Brenner, see also [7].

Table 14 Overview over all point measurements

Measurement point	Time	Weather (temperature, wind speed, wind direction and precipitation) from IUP weather station
Brückenstraße	Fr 22.06.18 14:05-15:15	20.4°C, 5.8m/s from northwest and no rain
	Mo 25.06.18 9:19-10:19	18.4°C, 2.3m/s from northwest and no rain
	We 27.06.18 12:01-13:02	26.9°C, 2.3m/s from north and no rain
	Fr 29.06.18 10:43-11:43	28.1°C, 1.5m/s from west and no rain
	Fr 29.06.18 15:54-17:00	34.0°C, 1.6m/s from north and no rain
Bismarckplatz	Fr 22.06.18 15:23-16:23	20.2°C, 6.0m/s from northwest and no rain
	Mo 25.06.18 10:24-11:24	21.2°C, 2.2m/s from northwest and no rain
	We 27.06.18 13:07-14:07	29.4°C, 3.9m/s from north and no rain
	Fr 29.06.18 11:49-12:53	30.5°C, 3.1m/s from east and no rain
	Tu 03.07.18 09:21-10:21	26.7°C, 1.0m/s from north and no rain

Neckarstaden/B37 near Marstall	Fr 22.06.18 16:34-17:37	20.2°C, 4.5m/s from north and no rain
	Mo 25.06.18 11:34-12:36	23.7°C, 2.6m/s from north and no rain
	We 27.06.18 14:16-15:18	31.8°C, 3.3m/s from north and no rain
	Fr 29.06.18 13:02-14:04	30.9°C, 3.2m/s from east and no rain
	Tu 03.07.18 08:05-09:05	22.6°C, 0.9m/s from north and no rain
Speyerer Straße	Fr 22.06.18 17:59-18:59	19.5°C, 4.7m/s from northwest and no rain
	Mo 25.06.18 13:08-14:10	26.2°C, 3.1m/s from northwest and no rain
	We 27.06.18 15:45-17:07	30.3°C, 3.5m/s from northeast and no rain
	Fr 29.06.18 08:10-09:16	20.7°C, 1.5m/s from southwest and no rain

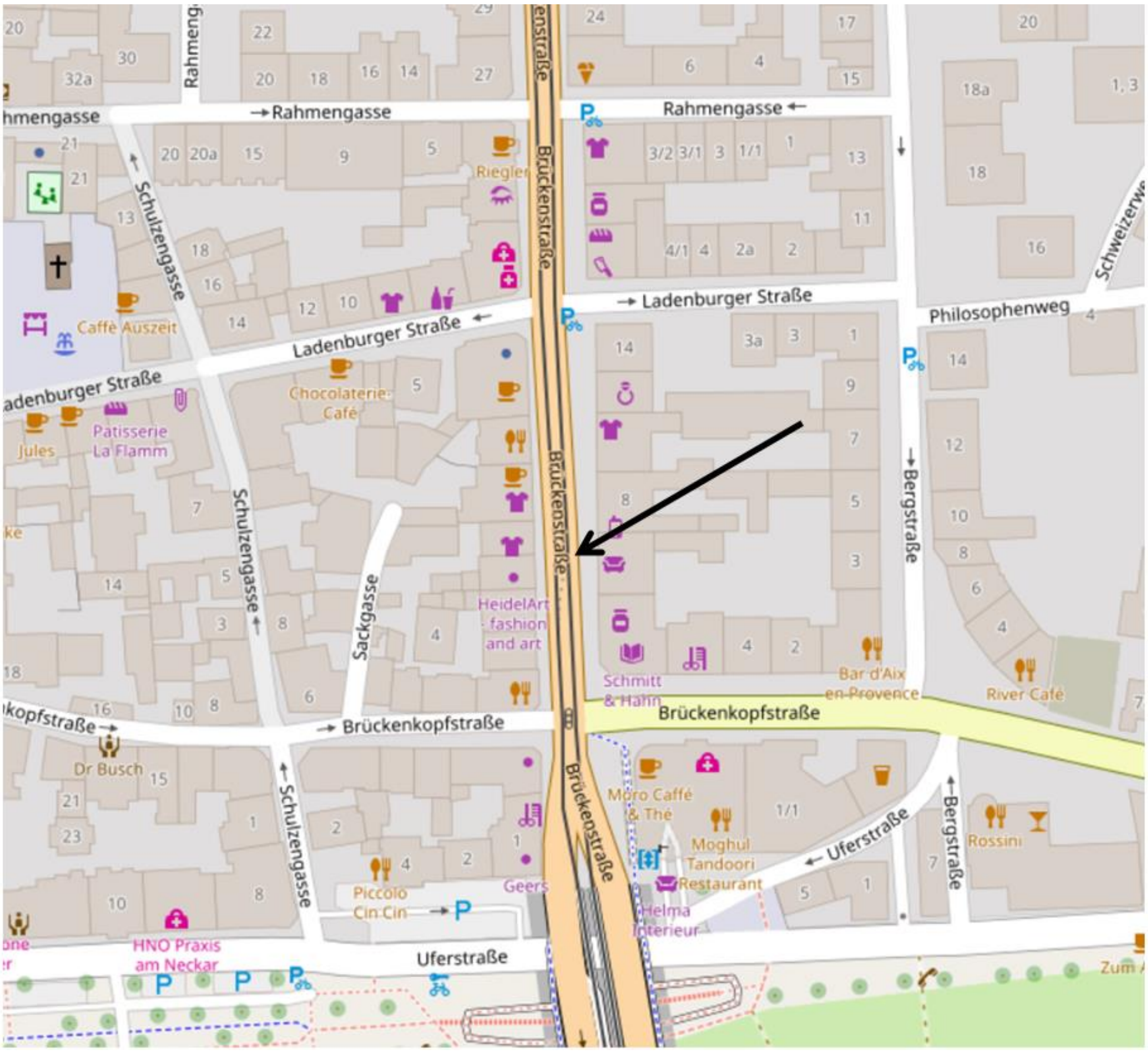

Figure 29 Map section of the point measurement site at Brückenstraße

Figure 30 Map section of the point measurement site at Neckarstaden/B37

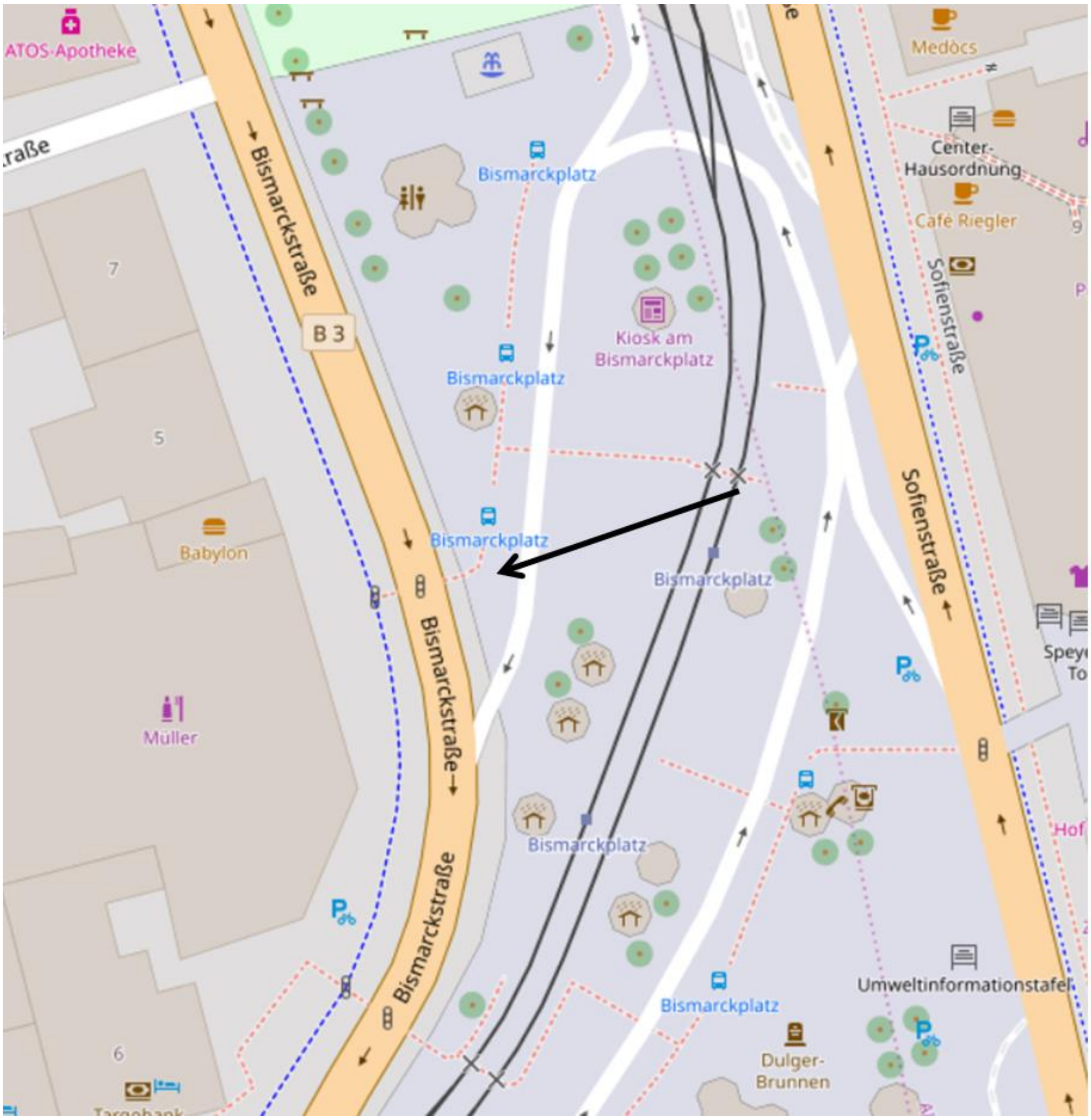

Figure 31 Map section of the point measurement site at the Bismarckplatz

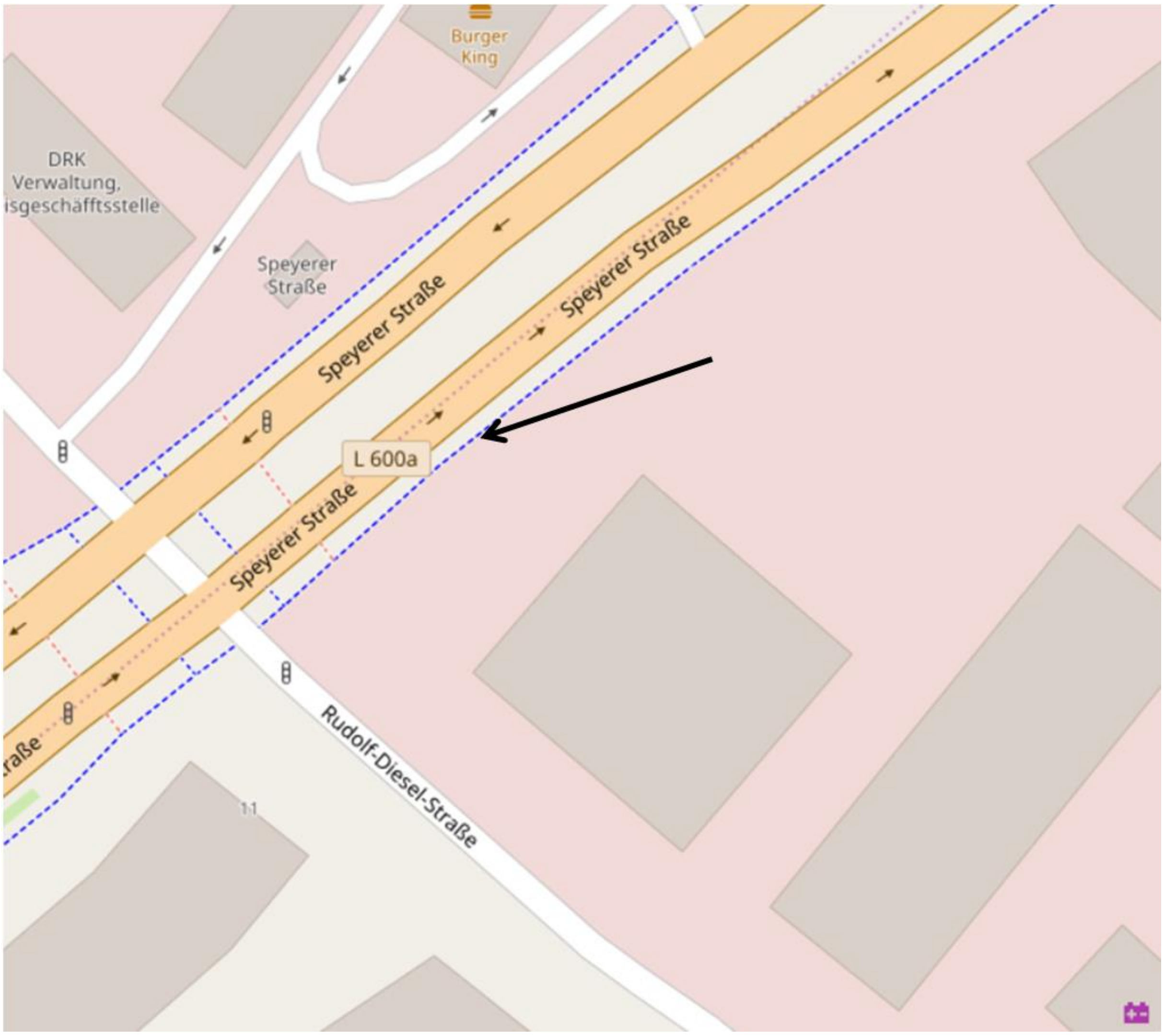

Figure 32 Map section of the point measurement site at Speyerer Straße

Table 15 Overview of the mean values and standard deviation for all point measurements. In the last line the mean concentration and standard deviation for all data points for each measurement point is given.

Brückenstraße			Bismarckplatz			Neckarstaden/B37 near Marstall			Speyerer Straße		
Date and time	Mean $[\frac{\mu g}{m^3}]$	Std $[\frac{\mu g}{m^3}]$	Date and time	Mean $[\frac{\mu g}{m^3}]$	Std $[\frac{\mu g}{m^3}]$	Date and time	Mean $[\frac{\mu g}{m^3}]$	Std $[\frac{\mu g}{m^3}]$	Date and time	Mean $[\frac{\mu g}{m^3}]$	Std $[\frac{\mu g}{m^3}]$
22.06 14:05-15:15	9	7	22.06 15:23-16:23	29	24	22.06 16:34-17:37	10	12	22.06 17:59-18:59	28	21
25.06 9:19-10:19	27	13	25.06 10:24-11:24	23	17	25.06 11:34-12:36	25	21	25.06 13:08-14:10	28	22
27.06 12:01-13:02	37	25	27.06 13:07-14:07	25	41	27.06 14:16-15:18	59	50	We 27.06 15:45-17:07	21	20

29.06 10:43-11:43	58	20	29.06 11:49-12:53	35	39	29.06 13:02-14:04	42	36	Fr 29.06 8:10-9:16	74	19
29.06 15:54-17:00	59	40	03.07 9:21-10:21	43	29	03.07 8:05-9:05	50	22			
Total mean values	38	21		31	30		37	28		38	20

Table 16 Overview of the average values and standard deviation for all point measurements, extrapolated to the annual mean. In the last line the mean concentration and standard deviation for all data points for each measurement point is given.

Brückenstraße			Bismarckplatz			Neckarstaden/B37 near Marstall			Speyerer Straße		
Date and time	Mean $[\frac{\mu g}{m^3}]$	Std $[\frac{\mu g}{m^3}]$	Date and time	Mean $[\frac{\mu g}{m^3}]$	Std $[\frac{\mu g}{m^3}]$	Date and time	Mean $[\frac{\mu g}{m^3}]$	Std $[\frac{\mu g}{m^3}]$	Date and time	Mean $[\frac{\mu g}{m^3}]$	Std $[\frac{\mu g}{m^3}]$
22.06 14:05-15:15	16	12	22.06 15:23-16:23	47	38	22.06 16:34-17:37	18	20	22.06 17:59-18:59	45	34
25.06 9:19-10:19	25	12	25.06 10:24-11:24	26	19	25.06 11:34-12:36	32	27	25.06 13:08-14:10	40	32
27.06 12:01-13:02	55	37	27.06 13:07-14:07	51	88	27.06 14:16-15:18	98	81	27.06 15:45-17:07	69	75
29.06 10:43-11:43	66	26	29.06 11:49-12:53	117	142	29.06 13:02-14:04	118	99	29.06 8:10-9:16	25	6
29.06 15:54-17:00	84	56	03.07 9:21-10:21	28	19	03.07 8:05-9:05	25	11			
Total mean values	49	29		54	61		58	48		45	37

Table 17 Coefficient c_{cms}/c_{ams} and standard deviation to convert measured NO_2 concentrations from annual means to means of certain daytimes and day types, differentiating between school time and school holiday as well as workdays and weekends. Here workdays include all days from Monday to Friday.

Time [hours, CET]	school time				school holidays			
	Workday		Weekend		Workday		Weekend	
	Coeff.	Std.	Coeff.	Std.	Coeff.	Std.	Coeff.	Std.
0	0.8	0.5	0.9	0.5	0.6	0.3	0.7	0.4
1	0.8	0.5	0.8	0.4	0.5	0.3	0.7	0.4
2	0.7	0.4	0.8	0.4	0.5	0.3	0.7	0.4
3	0.7	0.4	0.7	0.4	0.6	0.3	0.6	0.4
4	0.7	0.4	0.7	0.4	0.7	0.4	0.6	0.4

5	0.8	0.4	0.8	0.4	0.7	0.4	0.7	0.5
6	1.0	0.4	0.8	0.4	1.0	0.5	0.8	0.4
7	1.3	0.5	0.8	0.5	1.2	0.5	0.8	0.4
8	1.5	0.5	0.9	0.5	1.3	0.5	0.7	0.4
9	1.5	0.6	0.9	0.4	1.3	0.5	0.7	0.4
10	1.3	0.6	0.9	0.4	1.3	0.5	0.6	0.4
11	1.2	0.6	0.8	0.4	1.1	0.4	0.7	0.4
12	1.1	0.5	0.8	0.4	0.9	0.4	0.6	0.3
13	1.1	0.5	0.8	0.4	0.9	0.4	0.6	0.4
14	1.0	0.4	0.7	0.4	0.8	0.4	0.6	0.3
15	1.1	0.4	0.7	0.4	0.8	0.4	0.6	0.3
16	1.1	0.5	0.7	0.4	0.8	0.4	0.6	0.3
17	1.2	0.5	0.8	0.4	0.9	0.4	0.7	0.3
18	1.2	0.6	0.9	0.4	0.9	0.5	0.8	0.4
19	1.3	0.6	0.9	0.4	0.9	0.5	0.8	0.4
20	1.2	0.6	0.9	0.4	0.9	0.5	0.8	0.4
21	1.1	0.6	0.9	0.4	0.9	0.4	0.8	0.3
22	1.1	0.5	0.8	0.4	0.8	0.4	0.7	0.3
23	1.0	0.5	0.8	0.4	0.7	0.3	0.7	0.4

Table 18 Coefficient c_{ac}/c_{es} and standard deviation to convert measured NO_2 concentrations from annual means to means for each month.

Months	Coefficient	Standard deviation
January	1.0	0.6
February	1.0	0.6
March	1.1	0.6
April	0.9	0.5
May	0.7	0.5
June	0.7	0.3
July	0.9	0.5
August	0.7	0.4
September	0.9	0.4
October	1.0	0.4
November	1.2	0.4
December	1.1	0.5