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VERIFY

Observation-based system for monitoring and verification of

greenhouse gases

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Changes with respect to the DoA

Deliverable 2.7 was delayed due to:

- Delayed installation of in-situ and total column instruments (see MS8 report for further details)
- Instrument failure in Feb. 2020, repair at manufacture, re-installation delays due to COVID restrictions.

Dissemination and uptake

(Who will/could use this deliverable, within the project or outside the project?)

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Uptake:

- Evaluation of proxy/ffCO₂ ratios used in the TNO emission inventory (T2.1)
- Input to extend ¹⁴CO₂-based ffCO₂ estimates in T2.4.3.

Short Summary of results (<250 words)

In a metropolitan area located in South-Western Germany (Rhine valley), we have performed long-term measurements of CO, CO₂, NO_x, NO₂, and ¹⁴CO₂ using in-situ and remote sensing techniques. We investigated the atmospheric ratios of the in-situ proxy enhancements $\Delta CO/\Delta ff CO_2$ and $\Delta NO_x/\Delta ff CO_2$ as well as the total in-situ enhancements $\Delta CO/\Delta CO_2$ and $\Delta NO_2/\Delta CO_2$. Corresponding ratios of column-averaged abundances ($\Delta XCO/\Delta XCO_2$ and ΔNO_2 , $col/\Delta CO_2$) were derived from the remote sensing measurements and compared to the in-situ results. The range of proxy ratios determined for the total CO_2 enhancements agree between the in-situ and the total column observations. However, we can show significant changes in the in-situ proxy ratios when compared to $\Delta ffCO_2$ instead of total ΔCO_2 enhancements, highlighting the presence of non-fossil ΔCO_2 components. The in-situ $\Delta proxy/\Delta ff CO_2$ ratios are compatible with the assumption of a variable mix of different source sectors, assuming the TNO emissions ratios for each source sector. No clear seasonal or diurnal change of the proxy ratios (e.g. between heating and warm season) was found. This is because the spatial heterogeneity of the ffCO₂ sources around the KIT station causes more variations in the proxy ratios than their temporal changes. Simultaneous measurements of CO, NO_x and ${}^{14}CO_2$ provide three independent observables that might allow separating the ffCO₂ enhancements in the three main contributing sectors: industry, traffic and residential heating.

Evidence of accomplishment (report, manuscript, web-link, other)

Report



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1. Glossary

Abbreviation / Acronym	Description/meaning		
CO ₂	Carbon dioxide		
ΔffCO ₂	fossil fuel CO₂ enhancements		
¹⁴ CO ₂	Radiocarbon Dioxide		
AMS	Accelerator Mass Spectrometry		
CH ₄	Methane		
СО	Carbon monoxide		
CO ₂ MVS	CO ₂ emissions Monitoring and Verification Support		
COCCON	COllaborative Carbon Column Observing Network		
СРР	Coal fired Power Plant		
CRL	ICOS Central Radiocarbon Laboratory		
DMF	Dry air Mole Fraction		
DSCD	Differential Slant Column Density		
E-PRTR	European Pollutant Release and Transfer Register		
FCL	Flask and Calibration Laboratory		
ffCO ₂	fossil fuel CO ₂ concentrations		
FTIR	Fourier Transform Infrared (spectrometer or spectroscopy)		
GHG	GreenHouse Gases		
HEIPRO	Heidelberg Profile		
ICAD	Iterative CAvity enhanced DOAS		
ICOS	Integrated Carbon Observation System		
IMK-TRO	Institut für Meteorologie und Klimaforschung - Department		
	Troposphäre		
КІТ	Karlsruhe Institute of Technology		
LUBW	Landesanstalt für Umwelt Baden-Württemberg		
MAX-DOAS	Multi-AXis Differential Optical Absorption Spectroscopy		
N ₂ O	Nitrous oxide		
NO ₂	Nitrogen dioxide		
NOx	Nitrogen Oxides (NO ₂ +NO)		
SCIATRAN	radiative transfer model for SCIAMACHY		
STaLA	Statistisches Landesamt Baden-Württemberg		
тс	Total column		



TCCON	Total Carbon Column Observing Network
TNO	Toegepast Natuurwetenschappelijk Onderzoek(English: Netherlands Organisation for applied scientific research)
VCD	Vertical Column Density
VERIFY	VERIFYING GREENHOUSE GAS EMISSIONS
VOCs	Volatile Organic Compounds
WMO	World Meteorological Organization
XGAS	Dry air molar gas fractions, e.g. XCO ₂ , XCO



2. Executive Summary

Quantifying anthropogenic emissions from fossil fuel combustion (ffCO₂) on different spatial scales, from urban to global, is one of the grand challenges for the Paris Agreement. As CO₂ concentration measurements alone cannot distinguish between fossil and non-fossil CO₂ additional measurements of the isotopic CO₂ composition or observations of co-emitted species are common methods to estimate the fossil CO₂ share. This report brings together the isotopic and the co-emitted species approach for ffCO₂ estimates at one location where in-situ and remote sensing measurements are performed simultaneously. We apply the ¹⁴CO₂-method to derive insitu ffCO₂ enhancements and relate those to co-observed CO and NO_x concentration enhancements. On the one hand, these atmospheric $\Delta proxy/\Delta ffCO_2$ ratios will be compared to proxy/ffCO₂ emission ratios from the TNO emission inventory. On the other hand, we compare the in-situ $\Delta proxy/\Delta ffCO_2$ ratios to the remote sensing $\Delta X proxy/\Delta XCO_2$ ratios observed at the same location.

A strong motivation for the work we performed is the aspect that current and upcoming space missions are aiming at contributing to the quantification of anthropogenic fossil-fuel CO₂ emissions with global coverage, exploiting for this purpose the co-emitted species NO₂ and CO. We therefore have, using ground-based measurements, investigated in a test region in central Europe NO_x, NO₂, and CO and their correlations with ffCO₂. The selected region is located in the Rhine valley in South-Western Germany (Karlsruhe) and is characterized by a mixture of sources from different sectors embedded into agricultural and small forest areas. This complex structure can be regarded as an exemplary test case for urban agglomerations in Europe.

This study takes advantage of a wide suite of in-situ and remote sensing instrumentation which has been arranged by combining and exploiting existing observations in the selected area and merging these with additional sensors which have been enabled by VERIFY. The combination of in-situ and remote-sensing techniques allows the comparison of validated proxy/ffCO₂ data collected with the in-situ techniques on one hand with column-integrated remote sensing observations on the other hand. The remote sensing observations used here approximate the capabilities of upcoming space sensors (which will provide observations with high precision and small footprints).

We find that the in-situ measurements cover the expected range of variability of $\Delta NOx/\Delta ffCO_2$ and $\Delta CO/\Delta ffCO_2$, nicely reflecting the variable contributions of different source sectors (industry, heating, traffic). Especially, the industrial emission sector could be clearly identified using both proxies. The atmospheric $\Delta proxy/\Delta ffCO_2$ ratios from this sector agree well with the proxy emission ratios given in the TNO inventory. No clear diurnal or seasonal cycle can be established from the in-situ data. The expected seasonal cycle of the proxy/ffCO₂ ratios is masked at KIT station by the dominant spatial heterogeneity of sources with different proxy/ffCO₂ ratios. However, these source sector specific proxy/ffCO₂ ratios have potential to allow for a sectoral split of the observed fossil fuel enhancement. This could open the door for much enhanced collaboration with emissions inventory makers, as it would allow for sectoral attribution. Finally, this sectoral split is also requested by urban planners and decision-makers.



The remote sensing approach has no direct handle on $ffCO_2$, as variations in the CO_2 isotopologues are either inconclusive and / or too small to be detectable $(^{13}C/^{12}C)$, or the isotopologues are too rare for detection by remote sensing (¹⁴C). Therefore, we used the observed short-term variability of the column-averaged mixing ratios of NO₂, CO and CO₂ for separating signals originating from local sources. These signals are superimposed to the smoothly varying advected background abundances of the gases. The investigation of the short-term variability supports the determination of empirical correlations between the proxies and CO2. We find that the remote sensing measurements can detect significant variations between co-emitted species and carbon dioxide abundances, which is remarkable, as similar approaches based on temporal or spatial variability of observed columnar abundances would be applicable to spaceborne observations as well. However, the derived range of variability in the total column $\Delta X proxy / \Delta X CO_2$ abundances is significantly damped in comparison to the reference in-situ $\Delta proxy/\Delta ffCO_2$ results (by a factor of three to four), as we find that short-term variation of total CO2 is not a reasonable tracer for anthropogenic fossil-fuel emissions. The range of variability of the in-situ and the total column proxy ratios agree, however, if also for the in-situ observations the total CO₂ enhancement instead of the ffCO₂ enhancement ($\Delta proxy/\Delta CO_2$) is used. This shows that the short-term variability which is super-imposed on the averaged total column signal of CO₂ has a comparable fossil to non-fossil share as the total CO₂ enhancement of the in-situ measurement. We have thus to conclude that the short-term variability of the total column signal cannot be used to estimate the local ffCO₂ enhancement.

The main conclusion from the in-situ observations of our study is that within some limitations we detect the $\Delta proxy/\Delta ffCO_2$ ratios in the atmosphere as they are prescribed in the emission inventories. The combination of CO, NO_x and ¹⁴CO₂ provide three independent observables allowing us to principally separate the observed ffCO₂ enhancement in the three main source categories: industry, traffic and residential heating. The next challenging step will be to correctly account for the NO_x lifetime in this multi-proxy approach. Only once this is achieved, the multi-proxy approach can provide quantitative source sector separation. Atmospheric chemistry models and potentially auxiliary measurements of ozone and VOCs might be needed to develop this approach further. Until then the multi-proxy approach should be tested in urban settings where the variable NO_x lifetime is less of an issue as the time delay between emission and measurement is much shorter.



3. Introduction

Quantifying anthropogenic emissions from fossil fuel combustion (ffCO₂) on different spatial scales, from urban to global, is one of the grand challenges for the Paris Agreement. The Copernicus program is tackling this challenge by applying a holistic approach including components such as atmospheric space borne, ground-based in-situ and remote sensing measurements, bottom-up CO₂ emission maps, and modelling efforts of the carbon cycle in its anthropogenic CO₂ emissions Monitoring and Verification Support (CO₂MVS) capacity (Janssens-Maenhout et al., 2020). Separating CO₂ emissions into their fossil and non-fossil origins is obviously an important task for this. Radiocarbon observations of atmospheric CO₂ play hereby a key role. Due to their age, fossil fuels are void of radiocarbon and CO₂ emissions from their combustion lowers thus the natural ¹⁴C/C ratio in atmospheric CO₂, the so-called Suess-effect (Suess, 1955). Consequently, Radiocarbon is the most direct measure to separate non-fossil from fossil fuel CO₂ (e.g., Levin et al., 2003). In this context, the non-fossil CO₂ share includes different sources of CO₂ such as respiration by plants, soils, animals or humans and emissions from the combustion of biofuels.

Unfortunately, atmospheric ¹⁴CO₂ can still only be analysed on flask samples as no continuous ¹⁴CO₂ instrument with the necessary precision is currently available. Using ¹⁴CO₂-observations for total column ffCO₂ estimates might in principle be possible using air-cores (Chen H., 2016) but are extremely rare and most likely not scalable nor operationally feasible for the European CO₂ MVS.

Therefore, atmospheric trace gas species which are co-emitted along with fossil fuel CO_2 (ff CO_2) emissions such as CO and NO_x have been studied for decades and help to improve the ability of detecting ff CO_2 concentration enhancements (Δ ff CO_2) in the atmosphere. These co-emitted species are also called ff CO_2 proxies and are used for different purposes. In the following we list three examples of how proxies have been used to expand and improve the interpretation of fossil fuel CO_2 observations:

- Improve the temporal resolution of Δ ffCO₂ (Levin & Karstens, 2007)
- Sectoral attribution of Δ ffCO₂ (e.g., Turnbull et al., 2015)
- Spatial localization of $\Delta ffCO_2$ plumes, estimation of $\Delta ffCO_2$ from satellite measurements (e.g., Reuter et al., 2019, Konovalov et al., 2016)

These examples show how broad is the application range of $ffCO_2$ proxies. The fact that the proxies can be observed from space makes them particularly interesting for a global estimate of fossil CO₂ emissions. All proxy applications build on the co-emission of $ffCO_2$ and the proxies during the combustion of fossil fuels. CO and NO_x are the most commonly used $ffCO_2$ proxies. CO is produced during incomplete combustion of fossil fuel but also biofuels. NO_x has different formation pathways (1) by a thermal reaction between N₂ and O₂ (thermal NO), (2) by CHn radicals (prompt NO), or (3) from fuel nitrogen (Glaborg et al., 2017). According to Smooke et al. (1996), prompt NO is the dominant source of NO in hydrocarbon/air diffusion combustion. The production ratios of both proxies CO and NO_x depend thus on combustion temperature, efficiency



and fuel type. Therefore, different fossil fuel emission sectors have different proxy/ffCO₂ ratios, which may change over time for example due to technological improvements.

While for the time period of interest (a few hours to days) CO can be regarded as a stable proxy this is not the case for NO_x. NO_x has a complex and variable chemical lifetime depending on e.g., the NO_x concentration itself, OH, VOC and ozone concentrations as well as sunlight availability. Shah, V. et al. (2020) find lifetimes of NO_x to be 6 h in summer and 20 h in winter. During winter, NO_x lifetimes vary between 6 h during the night, and 30 h during the day (Kenagy et al., 2018).

This complex interplay of several parameters determining the proxy/ffCO₂ ratio in combustion and the additional difficulty of the variable atmospheric lifetime of NO_x reveal the fundamental challenge of any proxy approach to estimating $ffCO_2$. In order to better understand the uncertainties of the proxy-based $ffCO_2$ estimates, we pursue three questions in this VERIFY report:

- 1. How variable are proxy/ffCO₂ ratios we observe in the atmosphere, and can these variations be attributed to temporal or spatial changes in the composition of different emission sources?
- 2. Is the range of the atmospheric proxy/ffCO₂ ratios consistent with the proxy/ffCO₂ emission ratios in the TNO emission inventory?
- 3. How do the atmospheric in-situ proxy/ffCO₂ ratios compare with total column proxy/ Δ XCO₂ ratios?

Investigating these questions is relevant for assessing the emission ratios as currently represented in emission inventories on the one hand. On the other hand, the variability of the atmospheric proxy/ffCO₂ ratios provides important information that should be included in the inverse modelling of satellite proxy data.

In this context, we performed in the framework of VERIFY ground-based in-situ and remote sensing measurements for investigating in a test region in central Europe NO_x , NO_2 , and CO and their correlations with ffCO₂. The selected region is located in the Rhine valley in south-western Germany (Karlsruhe) and is characterized by a mixture of sources from different sectors embedded into agricultural and small forest areas. This complex structure can be regarded as exemplary test case for urban agglomerations in Europe.

In the following, we will firstly describe the measurement site and its surrounding from the perspective of an emission inventory, then describe the observational infrastructure, the observations performed, and the methods applied for the interpretation of data. We investigate the temporal variability of detected signals, interpret the results in terms of contributing emission sectors and compare results between in-situ and column-averaging remotely sensed data. A condensed discussion of our finding is provided in the final section "conclusions".



4. Temporal and sectoral variations of proxy/ffCO₂ ratios

The in-situ and total-column instruments operated at Campus North of KIT (near Karlsruhe, Germany; geographic coordinates 49.09°N and 8.43°E, altitude 110 m asl) and used for this study are presented in this section. Furthermore, we describe the surroundings of the KIT site and the main fossil fuel emitters therein.

4.1 In-situ instrumentation

The 200 m high tower of the KIT station allows conducting atmospheric measurements at platform levels of 200 m, 100 m, 60 m and 30 m height above local ground level (110 m asl). Within its role as ICOS atmosphere class 1 station, continuous measurements of CO₂, CH₄, N₂O and CO as well as meteorological parameters are conducted at all platform heights. In addition, in-situ ²²²Rn activity concentrations are measured at 200 m, 100 m and 30 m height and 1-week integrated ¹⁴CO₂ samples are collected at 200 m. The requirements of an ICOS class 1 atmosphere station are described in the ICOS Atmosphere Station Specifications document (ICOS RI, 2020). All ICOS class 1 atmospheric stations are equipped with an automated ICOS flask sampler to collect 1 hour averaged air samples in flasks to measure an extended set of Greenhouse Gas (GHG) concentrations and the isotopic composition of CO_2 and CH_4 and the atmosphere O_2/N_2 ratio. These flask samples are also used to quality control the continuous in-situ measurements. The ICOS flask sampling strategy is detailed in Levin et al. (2020). A comprehensive report on how the KIT station is compliant to the ICOS specifications is available in the KIT station labelling report (ICOS carbon portal, on request). All ICOS level-2 data and the near real-time (NRT) data can be obtained from the ICOS Carbon Portal (https://www.icos-cp.eu/data-services/about-dataportal).

In the scope of this project, we also conducted continuous in-situ NO_x (NO and NO_2) measurements at 200 m from July 2019 to August 2020 (see figure 1 for the data coverage). The NO_x concentrations have been measured with an ICAD (Iterative CAvity enhanced DOAS) system, which spectroscopically measures the concentration from characteristic absorption structures of NO_2 (Horbanski, 2019). Due to technical problems with the device, we do not have data for February and March, as well as for parts of May.

Besides the routine ICOS flasks we collected additional flask samples for ¹⁴CO₂ analysis in VERIFY at 200 m and at 30 m to determine the fossil fuel CO₂ contribution of the measured total CO₂ enhancements. All flask samples have been analysed for their GHG concentrations at the ICOS Flask and Calibration Laboratory (FCL) in Jena, Germany. CO₂ extraction and graphitisation for the subsequent ¹⁴CO₂ Accelerator Mass Spectrometry (AMS) measurements have been done at the ICOS Central Radiocarbon Laboratory (CRL) in Heidelberg, Germany, as further described in Lux (2018).





Figure 1: Data coverage of the different in-situ measurements. Coloured cells denote a data coverage of more than 50% on at least one sampling height during that month.

4.2 Total column instrumentation

In order to be able to measure the total column of the GHG's (XCO₂, XCO and XCH₄) and the trace gas NO₂ concentrations, two different techniques and three different instruments have been used, as described below.



Figure 2: Location of the instruments within KIT campus north. The in-situ measurements are performed at the KIT tower (A). The MAX-DOAS instruments are located at A and B. The EM27/SUN FTIR spectrometer is operated at position B. At position C, the TCOON instrument is located. The bottom panel shows a map of the Campus North (copyright KIT, North direction indicated) with positions A, B, C marked. Distances are AB = 1.2 km, AC = 1.7 km, BC = 0.8 km



4.2.1 Fourier Transform Infrared Spectrometers

The dry air column-averaged mole fractions, denoted XCO₂, XCO and XCH₄ are derived from solar absorption spectra collected by two different ground-based FTIR instruments.

- The Bruker IFS 125HR spectrometer: this high-resolution spectrometer is operated at KIT Campus North as part of the TCCON network. It is located at position C marked in Figure 1.
- The EM27/SUN spectrometer: This portable instrument serves as reference unit for the COCCON network and is set up each day of good weather conditions at position B marked in the figure above.

With both instrument the three species mentioned above can be measured with the main difference that the EM27/SUN has been developed more recently to be a portable and cheaper device than the IFS 125HR used by TCCON. It is a low-resolution spectrometer, which in practice does not limit the quality of the retrieved columnar abundances of greenhouse gases in comparison to TCCON.

The precision of the column-averaged abundances depends on the integration time applied, generally COCCON recommends to co-add ten double-sided interferograms recorded at 10 kHz sampling rate. This results in an integration time of one minute per measurement. From the co-added interferogram a spectrum is calculated and subsequently analysed for deriving the atmospheric trace gas contents. Typically, a precision (one-sigma empirical standard deviation) of 0.1 ppm for XCO₂, 0.3 ppb XCH₄, and 0.2 ppb for XCO is achieved under clear-sky conditions. Using Allan variance analysis to the measured column difference for co-located instruments, the precision of the differential column measurements was estimated by Chen and co-workers to be in the range of 0.01 % (Chen et al., 2016) for XCO₂ and XCH₄, a result even more favourable than the aforementioned estimates. Due to the much higher spectral resolution applied, the single measurement precision of TCCON is worse by about a factor of three to four for XCO₂ and XCH₄, while XCO benefits from the higher spectral resolution applied by TCCON. For XCO, the single measurement precision of TCCON therefore is comparable to the precision of COCCON.

The calibration accuracy with respect to WMO / in-situ units for TCCON and COCCON XCO_2 and XCH_4 data products have been shown to be within 0.2% for XCO_2 and XCH_4 (Sha et al., 2020). The calibration of the current TCCON XCO product generated with GGG2014 seems imperfect with a low bias of about 6% (Zhou et al., 2019). The absolute calibration of COCCON XCO is expected to be correct within 3% (Sha et al., 2020).



4.2.2 Multi-AXis Differential Optical Absorption Spectroscopy (MAX-DOAS)

The vertical column (VC) and the vertical profile (from which the near ground concentration is implicit) of NO₂ has been calculated from the measured spectra. In order to achieve this task, two ground-based MAX-DOAS instruments were installed at the rooftop of the Institute of Meteorology and Climate Research building and the other one at the rooftop of the IMK-TRO tower. Both instruments are located in B and A respectively in the figure 2. The azimuthal directions of the MAX-DOAS observations are indicated in figure 3.

Error estimation

This paragraph is based on the work by Sinreich (Sinreich, 2008) and Stutz and Platt (Stutz and Platt, 1996). The total measurement error budget is comprised of statistical and systematic contributions:

- Statistical error sources: Which is the noise produced by the incoming photons and the detection process. The first one is Poison distributed and therefore is proportional to the square root of the number of detected photons, while the last one is specific to the instrument's detector, which is mainly characterized by its dark current.
- Systematic error sources: There are several contributions, among which we can mention:
 - Not taking into account all the traces gases absorbing in a defined wavelength range used in the spectral fit, which creates uncertainty in the retrieval.
 - > Neglected temperature dependency of spectral cross-sections.
 - Inconsistency between the wavelength-pixel mapping of the instrument with respect to the calibration of the trace gases cross-sections.
 - Instrumental stray light and non-linearities.
 - Electronic offset of the detector

The retrieval errors used / calculated in this report are merely statistical, which in overall are estimated to amount \sim 10 - 15 %.





Figure 3: Geometry of the different azimuth angle directions measured with MAX-DOAS: 0 (North), 60, 120, 180 (South), 240 and 300.

4.3 KIT site surroundings

The KIT station is located in the densely populated and industrialised Upper Rhine Valley. The valley is 30 to 40 km wide and bordered to the west and east by the Odenwald and the Pfälzer Wald reaching altitudes up to 500 m higher than the enclosed valley bottom. As a consequence of this orographic situation, the Rhine Valley partly channels the wind directions leading to prevailing wind directions from SW or NE. The tower is on the south-western corner of the KIT Campus Nord, a large former nuclear research facility established 12 km north of the Karlsruhe city centre in a forested area (see figure 2). KIT Campus North (~ 4 000 employees) is causing local fossil CO₂ emissions and occasional emissions of ¹⁴CO₂ from the incineration of radioactive waste (BMUB, 2020). Direct ¹⁴CO₂ stack measurements for the waste burning facility are conducted by the KIT radiation protection division and available with weekly resolution. The greater surroundings of KIT tower encompass a complex mixture of multiple CO₂ sources and sinks which is, however, typical for a densely populated area. A heavily industrialised region is located 6 km to 16 km to the south-west of the KIT tower including a refinery with 15.5 Mt yr⁻¹ crude oil processing capacity, a 365 MW gas-fired power plant and a 1450 MW hard-coal-fired power plant (Hagemann et al., 2014). Figure 4b shows the surrounding map of KIT station overlaid with the fossil fuel CO₂ annual emission rates according to the TNO emission inventory for the year 2019 (Dellaert et al., 2019). The TNO inventory reports point and areal emission sources separately. For example, the point source ffCO₂ emissions from public power production or industrial activities are highlighted in figure 4b by the blue dots. The blue dots' different sizes relate to the ffCO₂ point



source strength as can be seen in the respective legend. Non-point source emissions as for example emissions from traffic and residential sources as well as point source below thresholds of 100 kton/a (CO_2), 500 ton/a (CO) and 100 ton/a (NO_x) are reported in the TNO inventory as areal sources aggregated to 1 km by 1 km grid cells. Areal and point source emissions are separated into 15 different emission categories in the TNO inventory (Dellaert et al., 2019). The gridded colour overlay in figure 4b shows the sum of all areal emission categories in the 1 km by 1 km resolution. Enhanced ffCO₂ emissions from areal sources are visible for densely populated areas like the city of Karlsruhe south of the KIT tower but also for areas with a large traffic volume like the A5 highway east of the KIT tower which runs in the north-south direction. Figures 4c and 4d show the total CO and NO_x emissions as the sum over all emission categories reported by the TNO inventory. When comparing the point sources in figure 4b to 4d, it is interesting to note that strong fossil CO_2 point sources coincide with strong NO_x point sources, but not with strong CO point sources. In the map shown in figure 4a, the forested areas are shown in dark green, whereas the light green areas represent agriculturally used land. Besides ffCO₂ emitters, the KIT surrounding also contains agricultural and forested areas constituting additional non-fossil CO₂ sources and sinks (Hagemann et al., 2014; Huang et al., 2019). Consequently, the station comprises a unique site where urban, industrial and rural (agricultural) emissions contribute to the measured signals. Local traffic emissions coming from a road close to the station have been reported by Shen X. et al. (2019).





Figure 4: Map of the KIT surrounding combined with the TNO emission inventory for $ffCO_2$, CO and NO_x. a) 45 km by 35 km overview map around KIT station with land use information. Dark green represents forests, light green agriculture and white urban areas. The coloured overlay (logarithmic scale) shows the spatial distribution of the annual emission rates of $ffCO_2$ (b), CO (c) and NO_x (d) in kg per year per grid cell. The blue dots represent annual point source emissions of single facilities, for example, power plants or refineries. Note that only strong single emitters are resolved as point sources, emissions from small facilities also contribute to the area emissions. The emission data are taken from the TNO inventory for 2019, the underlying map from (OpenStreetMap contributors).

4.4 Determination of atmospheric proxy/ffCO₂ ratios

In this section we describe the methods used for selecting atmospheric situations which have been predominantly influenced by local and regional $ffCO_2$ emissions. For those situations we illustrate how the $\Delta CO/\Delta ffCO_2$ and the $\Delta NO_x/\Delta ffCO_2$ ratios have been determined.

4.4.1 In-situ measurements

The basic idea for the determination of proxy/ffCO₂ ratios is based on comparing the measured concentration enhancements of a proxy and ffCO₂. Since in-situ ffCO₂ cannot be measured continuously, the fossil CO₂ concentration enhancement (Δ ffCO₂) must be determined based on collected flask samples using ¹⁴CO₂ measurements. ¹⁴C-based fossil-fuel CO₂ estimates use differential ¹⁴CO₂ measurements between a so-called "background" and a "signal" situation according to equation 1, which is adopted from Levin et al. (2011):

$$\Delta \text{ff} CO_2 = \frac{\text{CO}_{2,bg}(\Delta^{14}C_{bg} - \Delta^{14}C_{bg,nuc} - \Delta^{14}C_{bio}) - \text{CO}_{2,sig}(\Delta^{14}C_{sig} - \Delta^{14}C_{sig\,nuc} - \Delta^{14}C_{bio})}{\Delta^{14}C_{bio} + 1000\%}$$
(1)

where $CO_{2,x}$ and $\Delta^{14}C_x$ are the measured CO_2 concentration and its corresponding radiocarbon¹⁴C/C ratio expressed in Δ notation according to Stuiver and Polach (1977), for either the background (bg) or the signal (sig) situation. $\Delta^{14}C_{x nuc}$ accounts for the ¹⁴CO₂ contamination from nuclear facilities and $\Delta^{14}C_{bio}$ is the $\Delta^{14}C$ signature of the biogenic respiration flux. More details on the $\Delta^{14}C_{x nuc}$ corrections are given in Appendix A. The average change in ffCO₂ resulting from $\Delta^{14}C_{x,nuc}$ correction is 0.05 ppm, ranging from no correction at all to 1.13 ppm for individual flasks.

As mentioned in the description of the in-situ instrumentation, the ICOS flask samples represent the averaged atmospheric mixing ratios during the one hour of their collection. The proxy concentration enhancements can either be calculated using the corresponding proxy concentration measurements on the background- and the signal-flask, or, if no proxy measurements on the flasks are available, mean proxy mixing ratios can be calculated from the continuous in-situ proxy measurements.



Flask sampling cannot be done retrospectively. Thus predefined flask sampling strategies have to be developed. In this project, we applied two different flask sampling strategies to collect background and signal samples.

The first strategy is called the **"single-height" approach** further on. In the single-height approach, the background and the signal flask are collected from the same intake height level, which in the case of KIT tower was the 200 m level. The background flasks are sampled during situations with presumably low ffCO₂ influence, while the signal flasks are sampled during situations with strong ffCO₂ influence. Ideally, these two situations should be close in time. A classic example for applying the single height approach is the sampling of an exhaust plume at changing wind directions. The background flask is collected before the plume passes over the station while the signal flask is collected when the plume passes over the station.

Within the second sample strategy, named the **"dual-height" approach**, the flasks are taken at two different heights. The basic idea is to exploit the vertical concentration gradient during situations of reduced vertical atmospheric mixing. The background flask is collected at 200 m while the signal flask is taken at 30 m, sampling enhanced CO₂ concentrations resulting from the accumulated CO₂ emissions in the footprints of the 30 m intake height at KIT tower. The dual height approach was tested for late evening and early morning times based on considering that different emissions sectors have different diurnal emission profiles. Note that since we measure NO_x only at 200 m, the dual height approach results can only be used to calculate Δ CO/ Δ ffCO₂ ratios.

In figure 5, two typical examples for both sampling approaches are shown. Similar plots for all single-height flask pairs with all proxies available are compiled in appendix B. The consistent layout of these plots is as follows:

- The vertically shaded areas in all panels show the times during which flask samples have been taken. Green denotes a background flask (always at 200 m), signal flasks are either red (200 m) or blue (30 m) depending on the sampling approach used. The black symbols in the centre of the flask sampling period denote the mean concentration of the different species during the flask sample time, either obtained by measuring the concentration from the flask air (circular symbol) or the mean from the continuous measurements during flask sample time (squared symbol) and always relate to the left axis. The difference between signal and background leads to the concentration enhancement used to obtain the Δproxy/ΔffCO₂ ratios.
- ffCO₂ enhancements between signal and background flask are shown as a black bar in the CO₂ panel during the signal flask sampling time and refer to the right axis.
- The first two panels of figure 5 show the in-situ measured CO₂ and CO concentrations. The measurements for both species are conducted with one instrument for all intake heights shown in different colours (blue = 30 m, orange = 60 m, green = 100 m, red = 200 m). In routine operation, the intake heights are switched every five minutes, and the first minute of each measurement interval is flagged to account for flow instabilities and cross-sample



contamination. Four minutes of valid measurements are taken at each height, leading to gaps of 16 minutes between two consecutive measurements at the same height. For better visibility in the plot, the data points are depicted as line plots. After implementing the ICOS flask sampling strategy, the in-situ measurements remain every third day for 90 minutes at the 200 m level during noon to allow for better quality control of the measurements.

- Continuous NO_x and NO₂ are shown in the third panel of figure 5. Both measured semicontinuously (alternating every 40 seconds) at the 200 m level only. NO_x is given red, NO₂ in dark red.
- Wind speed at 200 m is given in the fourth panel.
- Wind direction at 200 m (red) and 30 m (blue) are given in the fifth panel. The upper horizontal blue shaded area denotes wind from SW, i.e. 220°-250° (industrial wind sector). The wind directions are defined as for the total column measurements: 0° (North), 90° (East), 180° (South), 270° (West).
- ²²²Rn activity concentrations for the different heights are shown in the sixth and last panel.

Figure 5a shows an example for the single-height approach where signal and background flask were sampled at the 200 m level on January 10, 2020. During the entire 24 h period, the wind direction is relatively stable from the South-Westerly wind sector in which the major industrial sources are located (see section "KIT surroundings"). The lower boundary layer is well mixed throughout this day, indicated by the small vertical CO₂ concentration differences between all levels. Between 11:30 and 12:30, a large CO₂ enhancement of about 30 ppm was observed, accompanied by a small CO enhancement of only 10 ppb and a NO_x enhancement of about 15 ppb. A background flask was taken between 09:00 and 10:00 in the absence of the CO_2 peak. The signal flask collected between 12:00 and 13:00 contains about half of the CO₂ signal peak. Using equation 1, these two flasks can estimate the $ffCO_2$ share of the observed CO_2 enhancement. 25.9 ± 1.1 ppm out of the 26.1\pm0.1 ppm total CO₂ enhancement were of fossil origin. This substantial Δ ffCO₂ peak is accompanied by a CO enhancement of 14.1±1.4 ppb and Δ NO_x of 8.5±0.1 ppb. All uncertainties are reported as 1-sigma uncertainties of the concentration differences. The individual uncertainties of the background and signal concentrations are based on the uncertainty of the flask concentration measurements or the in-situ analysers' measurement precision. The uncertainty of Δ ffCO₂ is dominated by the long-term ¹⁴CO₂ reproducibility of 2.3 ‰.

The concentration enhancements are used to calculate the Δ CO/ Δ ffCO₂ and Δ NOx/ Δ ffCO₂ ratios to 0.54±0.06 ppb/ppm and 0.33±0.01 ppb/ppm, respectively. Both ratios are small, suggesting a clean ffCO₂ source with small CO and NOx co-emissions typical for emissions from the coal-fired power plant (CPP) emitting at 200 m in about 10 km distance. The emission ratios for this specific CPP are <0.20 ppb/ppm and 0.45 ppb/ppm according to the E-PRTR pollution register (E-PRTR, 2020). Note that E-PRTR does not report CO emissions from the CPP, indicating that its yearly emissions lay below the threshold of 500 t. Using this threshold value, the ratio given here is only an upper boundary value. The measurement and the E-PRTR emission ratios do not agree, which might indicate that we are not only measuring this single CPP plume.





Figure 5: Two examples of situations, where flask sample pairs (signal and background) were sampled, at January 10, 2020 (a) and March 13, 2020 (b). In both cases, the uppermost panel shows the continuous measurements of CO₂, followed by CO in the second panel, and then NO_x, wind speed and direction and radon measurements, each referring to the specifications given at the left axis. The colours denote the sampling heights as given in the legend. For detailed description of the plot please refer to the main text

Figure 5b is an example of the dual-height approach sampled on March 13, 2020. The background flask is taken at 200 m from 20:00 to 21:00, while the signal flask is collected at 30 m from 22:00 to 23:00. As in example a, we have a well-mixed lower boundary layer during the morning and



the afternoon, indicated by the concurrent CO_2 and CO concentrations at the different measurement heights. In the beginning of the evening at 17:00, the concentrations of all species at the lower intake heights start to increase due to the reduced atmospheric vertical mixing. The development of the stratified lower boundary layer is also accompanied by reduced wind speeds at all heights (only the 200 m level is shown in the plot). The concentrations at the 200 m level remain rather stable until 23:30. As the night progresses, the nocturnal accumulation of CO₂ and CO remains for the lower intake heights, while the CO_2 signal at 200 m shows strong variations which are probably due to the exhaust plume of the coal power plant in 200 m. The background flask was taken at 200 m from 20:00 to 21:00 and still represents air similar to the well mixed atmospheric conditions of the afternoon, while the signal flask at 30 m from 22:00 to 23:00 contains air which has been influenced by local sources in the surrounding of the KIT tower. Different to example a, the $ffCO_2$ enhancement between signal and background is only 5.0±1.2 ppm out of the total CO₂ enhancement of 12.1 \pm 0.1 ppm. Combined with Δ CO = 86.2 \pm 4.2 ppb, this leads to a $\Delta CO/\Delta ff CO_2$ ratio of 17.37±4.42 ppb/ppm, indicating an emission source with a $\Delta CO/\Delta ff CO_2$ ratio different than the industrial signal in example a. With the start of the nocturnal stratification and thus the GHG accumulation period the wind direction of the 30 m level changes to southern directions. No NO_x data is available for example b due to instrument maintenance. Since NO_x observations are available at 200 m only, we generally cannot derive $\Delta NO_x/\Delta ff CO_2$ ratios for the dual-height approach.

For the subsequent analysis, we rejected data according to two following criteria:

- relative error of the $ffCO_2$ enhancement is larger than 50%. The analytical ¹⁴CO₂ error is the dominate source of uncertainty in the calculation of the $\Delta proxy/\Delta ffCO_2$ ratios and independent of the magnitude of the $\Delta ffCO_2$ signal
- either the signal or the background flask sampling was influenced by wind from the 0°-90° (KIT area) during weeks where artificial ¹⁴C emissions from the KIT area are reported.



4.4.2 Total column measurements

To measure XCO_2 and XCO we use FTIR observations, and to measure vertical profiles of NO_2 for obtaining so-called Vertical Column Densities (VCDs) we use the MAX-DOAS technique. To account for differences in these two techniques we use two different approaches to detect local emission signals. The retrieval procedures applied for the FTIR and the MAX-DOAS measurements are briefly explained below:

- FTIR: The raw data are collected either with the IFS 125R spectrometer in the framework of TCCON or with the EM27/SUN spectrometer in the framework of COCCON. Both kinds of spectrometers generate DC-coupled interferograms (a signal proportional to the actual photocurrent is recorded) as resulting from direct solar observations. These interferograms are converted into spectra by applying a DC-correction and a subsequent Fast Fourier Transform. These spectra serve as input for the final analysis performed with a retrieval algorithm (GFIT and PROFFAST are used respectively for the TCCON and COCCON data processing). The retrieval code scales the climatologically expected atmospheric trace gas profile (the so-called a-priori profile) for achieving the best spectral fit between the measured and a simulated spectrum. Using the resulting scaled version of the a-priori profile, the total column is calculated as integral over the target gas molecular number density along the atmospheric altitude coordinate. By applying the co-observed column of molecular oxygen, the target gas column is converted into the sought-after column-averaged dry air mole fraction (DMF). Use of DMFs reduces the effect of variable ground pressure and humidity on the reported abundances. More information regarding the FTIR data analysis and the retrieval algorithms used can be found in Kiel et al. (2016) and Sha et al. (2020), respectively.
- MAX-DOAS: The raw data collected with this instrument are spectra of scattered sunlight. In contrary to direct solar absorption spectra (the line of sight needs to point towards the sun), such spectra can be recorded along different selected elevations and azimuthal angles. Covering a range of azimuthal angles allows to estimate trace gas distributions with vertical and in addition even some horizontal resolution. While in case of an idealized horizontally isotropic atmosphere, the retrieved trace gas profile is expected to be the same for all directions, horizontal gradients might be detectable by the MAX-DOAS technique, if, e.g., a plume is advected from a nearby source and induces strong horizontal structures in the trace gas distribution.

Several corrections need to be applied on the raw spectra (bias correction, subtraction of dark current, correction of non-linear effects, etc.). Then, a non-linear least square algorithm is applied on the corrected spectrum in the so-called DOAS fit procedure. This requires several inputs: specification of the fitting interval where the target gas is absorbing, a polynomial number between 3 to 5 which mathematically represents the



broad band of the absorption cross-sections, the Mie and Rayleigh scattering, and the absorption cross-sections of all the trace gases that are absorbing in that interval. The details of the DOAS fit are discussed in in Platt and Stutz, 2008 . For a defined azimuth angle, the result of the fit is the Differential Slant Column Density (DSCD), which is the reconstructed concentration of the trace gas along the light path (which is a slant line). The DSCD calculated with the DOAS fit serves as input for the vertical retrieval algorithm, here the Heidelberg Profile (HEIPRO) has been used. HEIPRO uses SCIATRAN as forward model and it is based on Optimal Estimation Methods. It uses a two-step approach. In the first step, the aerosol extinction profile is derived by using the O₄ DSCD as measurement vector. In the second step the trace gas profile is derived by using the result of the previous step (aerosol profile) and the retrieved trace gas DSCD as a vector. Geometric correction delivers the vertical column density vector and integration over altitude the VCD. More details on HEIPRO can be found in Selami, 2012.

4.4.2.1 Deriving approximated proxy/ffCO₂ ratios from remote sensing measurements

Because there is no direct handle on ffCO₂ from remote sensing observations, the measured variability of the column-averaged trace gas abundances is used for achieving an approximative separation between nearby, strong, and localized fossil fuel emissions and other kinds of signals. The underlying rationale is that the variability on short intra-day time scales of XCO₂ is assumed to be dominated by local and regional sources and therefore short-term variations in XCO₂ can be regarded as approximation for ffXCO₂.

The NO₂ vertical column amounts calculated from the MAX-DOAS observations and the XCO total column amounts from TCCON observations, respectively, are used in the following for constructing the proxy signal in the $\Delta proxy/\Delta XCO_2$ ratios discussed in this section. In order to effectively separate the short-term fluctuations for both total column signals from longer-term variations, two different methods have been applied for XCO and XCO₂ on one hand and NO₂ on the other hand. This is enforced by the fact that the cadence of measurements is significantly lower for the MAX-DOAS than for the TCCON measurements (MAX-DOAS: one per hour, TCCON: one per several minutes), therefore we need to coarsen the procedures used for the TCCON measurements:

1. $\Delta XCO / \Delta XCO_2$

For calculating the short term deviations for both species, a median filter, with a 30 min window length, has been applied to the XCO and XCO₂ daily time series. The median filter's window length was appropriately adjusted to dampen variations of two hours duration and is shown as red stars in figure 6 in the top panels for XCO₂ and XCO for an example day. This smoothed version of the time series is assumed to approximate the average CO₂ concentration, which is slowly variable due to superimposed advected signals from various distant sources (and sinks) and due to variations associated with variable meteorological conditions. The imprints of local signals are suppressed in the smooth curve, as these local contributions tend to be variable on shorter time



scales (in response to changes of wind direction, vertical exchange, etc.). So we regard $\Delta X gas = X_{individual} - X_{gas,median}$ as a proxy for the local signals for ΔXCO and ΔXCO_2 .

2.
$$\Delta NO_{2,VCD}/\Delta XCO_2$$

In order to calculate ΔNO_2 VCDs, the daytime mean has been taken as reference value and then is subtracted from each individual point. It is important to note that because NO₂ VCD results are only hourly available while the cadence of the FTIR measurements is in the order of several minutes, the median filter method used for the FTIR data is not applicable for the MAX-DOAS data. Fortunately, due to the shorter atmospheric lifetime of NO₂ the contribution of local signals in comparison to advected background is much higher for NO₂ than for the other gases, so this coarser treatment enforced by the measurement procedure seems acceptable.

One might assume that in this situation an analogous treatment of XCO_2 appearing in the denominator of $\Delta NO_2 / \Delta XCO_2$ (using the daily mean as background) might achieve a better match. But it turns out, that the NO₂ approach adopted for XCO_2 would introduce significant amounts of background variability in the signal part, the reason for this being the very different lifetime of the two gases. We believe that the analysis approach as described above is the best what can be achieved on the grounds of the available observations.

MAX-DOAS measurements are available in 6 different azimuth angle directions, which means having ~ hourly profile and VCD in each azimuth direction starting at 06:00 and ending at 18:00 while TCCON results are related to the slant column from the direct sunlight observation (the spectrometer needs to track the solar position during the whole day). The FTIR measurements are available usually from 10:00 to 18:00 local time. According to the statements above, TCOON results (XCO₂) are shorter in their daily time coverage (while they achieve higher sampling rates than the MAX-DOAS). Another important point is that with TCCON the part of the atmosphere that is sampled is changing as prescribed by the solar azimuth angle (SAA); therefore, in order to compare the part of atmosphere that had been sampled with both instruments the following matching procedure has been applied:

- 1. XCO₂ is taken as reference for the time gridding,
- 2. The SAA from the TCCON observations serves as reference for determining which azimuth directions from MAX-DOAS are taken into account to match with a selected TCCON observation.
- 3. A time gridding is used to match with the start and end of the time range as prescribed by TCCON. Finally, time intervals fine enough to preserve the temporal resolution of the MAX-DOAS is selected.
- 4. All the NO₂ VCDs within the (mentioned above) time and SAA range are averaged and the results presented as a combined NO₂ VCD, which is interpreted as the most representative NO₂ VCD to be associated with the given set of TCCON XCO₂ results.



In order to classify the short-time variations of the total column for both gases, daily correlation plots between both gases are used. R^2 values > 0.5 in the linear regression are assumed to indicate significant events. Figures 6 and 7 demonstrate the data analysis for an example day.



Figure 6: Graphic representation of the methods used for the delta calculation for each gas by using 02.04.2020 as example. In the uppermost and middle plot, the median is used for defining the slowly variable average CO₂ concentration (red stars). In addition, the individual measurements (blue points) are shown. In the third plot (up-to-down), the composed NO₂ VCD (black dashed line) and the NO₂ VCD for all available azimuth angles are shown. In the lowermost panel, the hourly averaged wind velocity is shown. The local time zone (CEST) is ahead of UT by two hours.





Figure 7: In the left panel the resulting correlation plots for both proxies with respect to ΔXCO_2 can be seen for the example day 02.04.2020. In the right panel the wind rose for that day is presented.

4.5 Temporal variability of proxy/ffCO₂ ratios

Due to the different seasonality of the anthropogenic CO₂ sources (e.g., residential heating) and the different diurnal patterns of individual emission contributions (e.g., traffic rush hours), temporal variability in the averaged and weighted emission ratios are to be expected. This section examines if seasonal and diurnal variations of the atmospheric proxy/ffCO₂ ratios can be detected for the in-situ and the total column measurements.

4.5.1 In-situ measurements

In figure 8 the Δ CO and Δ NO_x to Δ ffCO₂ ratios are plotted over the time of one year, from July 2019 to July 2020 to investigate potential seasonal variations of the atmospheric proxy/ffCO₂ ratios. To distinguish between the two flask sampling strategies, the single-height approach is shown in red, while the dual-height approach is plotted in blue. As mentioned before, Δ NO_x/ Δ ffCO₂ ratios are only available in the single-height approach. Measurements taken during the winter period (October to March) are shown as dots, the ones form the summer period (April



to September) as crosses. No clear seasonal cycle is apparent from the data in either $\Delta CO/\Delta ff CO_2$ or $\Delta NO_x/\Delta ff CO_2$ ratio. As KIT tower is strongly influenced by industrial emissions from the South-Westerly wind sector, these might mask a potential seasonality in the $\Delta proxy/\Delta ff CO_2$ ratio of other source sectors. Therefore likely industrially influenced measurements have been plotted in light grey in Fig. 8. They have been classified by wind directions (between 220° and 250°) and the typical pattern in the in-situ time series like substantial enhancements and variations in CO₂ at 200 m as well as in NO_x, whereas CO remains without strong signals as shown in figure 5a. The red points should thus be dominantly influenced by the traffic and the heating sector. To guide the eye to see the TNO inventory predicted seasonal and diurnal variations in atmospheric proxy/ffCO₂ ratios, we calculated the inventory-based seasonal and diurnal cycles of the proxy/ffCO₂ ratios considering the traffic and the heating sector only (since we assume that industrially influenced ratios have been excluded in the selection before) around KIT station. The TNO emissions for both sectors in a 45 km x 35 km area around KIT (area shown in figure 4) result in $CO/ffCO_2$ ratios for the traffic sector of 6.6 ppb/ppm and 6.1 ppb/ppm for the heating sector. For $NO_x/ffCO_2$ the ratios are 2.5 ppb/ppm and 0.6 ppb/ppm for traffic and heating, respectively. TNO provides an average seasonal and diurnal cycle for the emissions of each emission sector. The red lines in the CO/ffCO₂ and NO_x/ffCO₂ plot of figure 8 show the variation between those two ratios with respect to the relative seasonal change of the heating and traffic emissions.

Since for CO/ffCO₂ both ratios are very close to each other, 6.6 ppb/ppm and 6.1 ppb/ppm, the expected change during the year is negligible and the red line does not show any variations. The nevertheless existing variations within our measurements towards lower ratios could be explained through an unconsidered industrial influence, not detected by our selection process. The higher ratios from the dual-height approach (shown in blue) could also result from an unaccounted industry influence in the background sampling at 200 m, leading to a higher ffCO₂ share and therefore a smaller ffCO₂ enhancement.

In the NO_x ratios, the TNO inventory-based ratios differ more, leading in summer to a shift to the dominating traffic ratios and in winter towards the lower heating ratio. The measurement NO_x/ffCO₂ ratios scatter between 0.2 ppb/ppm and 2.0 ppb/ppb. The lower ratios could again be explained through an unconsidered industrial influence, not detected by our selection process.

Figure 9 shows diurnal variations of the proxy to ffCO₂ ratios. Similar to figure 8, the different sampling approaches as well as the industrial influenced measurements are indicated by the red, blue and grey. Similar to the seasonal cycle in figure 8, the red lines in figure 9 shows the diurnal variations of the inventory-based ratios. Here, the diurnal cycles additionally are distinguished between winter (continuous line) and summer (dashed line) by scaling the cycles with only the winter (December, January, February) or summer (June, July, August) ffCO₂ emissions.

As before, due to the closely matching ratios, in $CO/ffCO_2$ no cycle is observable, whereas in $NO_x/ffCO_2$ a mix between the diurnal cycles of traffic and heat is observable, which though cannot be regarded as significantly followed by the measurements.

Using all our measurements for the $\Delta proxy/\Delta ffCO_2$ ratios, a significant seasonal or diurnal cycle was not detectable for any proxy. Instead, at the KIT station, spatial and thus, in first order, sectoral variability is much more dominant than temporal variability. This can be seen, for



example, in the strong variability of the $\Delta \text{proxy}/\Delta \text{ffCO}_2$ ratios determined at 22:00. The dualheight approach (blue) has a significantly smaller footprint than the single-height approach (red). All dual-height $\Delta \text{CO}/\Delta \text{ffCO}_2$ ratios >10 ppb/ppm were observed in winter (Nov. 2019 to April 2020). We assume that in winter at 22:00, the residential heating sector emissions are the dominant sources in the near field of the KIT station. As described in Deliverable Report D2.8, $\Delta \text{CO}/\Delta \text{ffCO}_2$ emissions from the residential heating sector are highly variable depending on the fuel used. The usage of biofuels (wood or pellets) in the residential heating sector is responsible for a large share of the CO/ffCO₂ variability as it emits only CO without ffCO₂. This variability would be a potential explanation for the variability observed here.



Figure 8: Seasonal variations of the $\Delta proxy/\Delta ffCO_2$ ratios. Upper panel: $\Delta CO/\Delta ffCO_2$ ratio over the months of the years 2019/2020. Lower panel: $\Delta NO_x/\Delta ffCO_2$ ratio over the months of the years 2019/2020. Red denotes that both samples, signal and background, have been taken at 200 m, blue denotes a signal sample taken from 30 m. Grey dots are samples probably influenced by emission from the industrial sector with mean wind directions between 220° and 250° and typical pattern (see figure 5a). Dots denote measurements in winter period, crosses in summer. The red line gives the seasonal change in the combination of the traffic and heat ratios as given from TNO.





Figure 9: Diurnal variations of the $\Delta proxy/\Delta ffCO_2$ ratios. Upper panel: $\Delta CO/\Delta ffCO_2$ ratio over the hour of the day. Lower panel: $\Delta NO_x/\Delta ffCO_2$ ratio over the hour of the day. Red denotes that both samples, signal and background, have been taken at 200 m, blue denotes a signal sample taken from 30 m. Grey dots are samples probably influenced by emission from the industrial sector with mean wind directions between 220° and 250° and typical pattern (see figure 5a). Dots denote measurements in winter period, crosses in summer. The red line gives the diurnal change in the combination of the traffic and heat ratios as given from TNO, for the continuous line scaled with ffCO₂ winter emissions (December, January, February), for the dashed line scaled with the summer emissions (June, July, August).



4.5.2 Temporal variations in the total column $Proxy/\Delta XCO_2$ ratios

To investigate the temporal variability of the total column $\Delta proxy/\Delta XCO_2$ both ratios have been treated as independent phenomena, and the requirement of achieving a R² >0.5 based on the correlation analyses is used as threshold for a reported event. Figures 10 and 11 show the time series of $\Delta XCO/\Delta XCO_2$ and of $\Delta NO_{2,VCD}/\Delta XCO_2$, respectively. The range of variability indicated by the remote sensing data overall seems reduced when compared to the in-situ results, we will discuss this finding further in the section "Comparison of proxy/ffCO₂ ratios derived from in-situ and total column data". Otherwise, the structure of the variability resembles the in-situ data: distinct enhancements are seen occasionally, but without clear prevalence of this happening during a certain season (a slight tendency of elevated values in $\Delta XCO/\Delta XCO_2$ during the winter season might be apparent – this would be in line with the expected increased share of residential heating). We do not attempt to derive a daily cycle based on the remote sensing measurements, because these measurements can only be taken while the sun is above the horizon and because the temporal resolution of the remote sensing data is low (measurement cadence MAX-DOAS is one hour, median filter length is in the order of one hour).



Figure 10: Time series for all the correlations with R² >0.5 in the period September 2014 to October 2020, for $\Delta XCO / \Delta XCO_2$



Figure 11: Same as figure 10, but for $\Delta NO_{2,VCD}/\Delta XCO_2$



4.6 Sectoral variability of proxy/ffCO₂ ratios

In the previous discussion of the temporal variability of proxy ratios as observed by in-situ instrumentation at KIT we concluded that the temporal variability of the in-situ proxy/ffCO₂ ratios could not be observed as the spatial heterogeneity of emission sources superimposes a large additional variability on the proxy/ffCO₂ ratios. In the following, we try to benefit from these circumstances by investigating the atmospheric proxy/ffCO₂ ratio of the industrial sources. Several industrial sources are located in the South-Western wind sector and their emissions lead to characteristic patterns in the continuous observations (see figure 5a). These presumably industrially dominated atmospheric proxy/ffCO₂ ratios are compared to the industrial emission proxy/ffCO₂ ratios reported in different emission inventories. Furthermore, we investigate if and to which degree observed proxy/ffCO₂ ratios from other, non-industrial wind sectors, can be explained by different shares of the three main emission sources traffic, residential heating and industry.

4.6.1 Proxy/ffCO₂ ratio for different emission sectors and fuel types

Before looking at the actual measured data, we provide an overview on the variability of the proxy/ffCO₂ ratios in different emission inventories for south-west Germany. In the following, additional to the TNO inventory from 2019 and 2015, reported emissions and their ratios of two other inventories are presented for comparison. Both alternative inventories are led by the federal state of Baden-Württemberg. One is from the "Landesanstalt für Umwelt Baden-Württemberg" (LUBW, 2020), the other one is from "Statistisches Landesamt Baden-Württemberg (STaLA, 2020).

To make the ratios from the inventory emissions comparable to concentration measurements, they need to be converted from kg/kg to ppb/ppm, which can be done by dividing by the molecular weights of the species. For CO/ffCO₂ this gives a factor of 44/28 and 44/46 for NO_x/ffCO₂ respectively, as the NO_x emissions are reported in kg of NO₂ [pers. communication, H. Denier van der Gon, (2020)].

In table 1, reported annual emissions for 2014 (LUBW, CO from STaLA), 2015 (TNO, CO₂ and NOx from STaLA) and 2019 (TNO) respectively, of CO₂, CO and NOx are shown for the three sectors industry, traffic and heating in whole Baden-Württemberg¹.

The reported absolute emissions for the individual sectors are differing by factors of up to 2. However, the overall $ffCO_2$ emissions for all sectors differ by at most 5% between the three inventories, meaning that their disaggregation to the individual sectors is diverging. The large

¹ For the TNO emissions, industry is defined as the TNO source sectors A and B, traffic by the sectors F1-F4 and heating by sector C for a spatial region which is approximately comparable to the extent of the state of Baden-Württemberg. The LUBW sectors are taken as follows: "Industrie" for industry, "Straßenverkehr" for traffic and "Brenngase", "Heizöl" and "Festbrennstoffe" for heating

In StaLA, industry comes from "Industrie, Feuerungen und öffentliche Kraftwerke", traffic from "Verkehr (ohne Internationalen Flugverkehr)" and heating from "Private Haushalte, GHD, übrige Verbraucher".



differences on the sectoral level could partly be related to not having the same categories for the source sectors. However, the resulting proxy/ffCO₂ ratios agree mostly well. Big differences appear in the CO/ffCO₂ ratio from STaLA relatively to the one from TNO₂₀₁₉ with ratios of 11.2 ppb/ppm and 6.45 ppb/ppm, respectively, and also in the CO/ffCO₂ of the traffic sector. While STaLA and TNO2019 agree well with ratios of 7.15 ppb/ppm and 7.41 ppb/ppm, LUBW reports a ratio of 10.87 ppb/ppm. These disagreements between the different inventories show one reason why it is indispensable to investigate those emission ratios experimentally. This becomes even clearer, as the preliminary experimental findings from the traffic campaign in Heidelberg (see D2.8) suggest a mean CO/ffCO₂ ratio of 11.7±1.4 ppb/ppm, which agrees within its uncertainty with the traffic ratio reported by LUBW.

Inventory	Sector	CO/ffCO2 [ppb/ppm]	relative change to TNO2019 [%]	NOx/ffCO2 [ppb/ppm]	relative change to TNO2019 [%]
TNO	industry	1.71		0.97	
(2019)	heating	6.45		0.63	
	traffic	7.41		2.38	
TNO	industry	1.52	-11	0.97	0
(2015)	heating	6.96	8	0.63	0
	traffic	7.64	3	2.53	6
LUBW	industry	1.29	-25	0.71	-26
(2014)	heating	7.52	17	0.63	0
	traffic	10.87	47	2.32	-3
STaLA	industry	1.23	-28		
(2014/15)	heating	11.20	74		
	traffic	7.15	-4	3.15	32

Table 1: $CO/ffCO_2$ and $NOx/ffCO_2$ ratios from three different inventories and for different years, each for the emission sectors industry, heat and traffic. The column after the ratio $CO/ffCO_2$ or $NO_x/ffCO_2$ respectively, gives the relative change with respect to the values from the TNO inventory from 2019.

4.6.2 Comparison of atmospheric and inventory proxy/ffCO2 ratios

Figure 12, further referred to as the "double-ratio plot", shows the $\Delta NO_x/\Delta ffCO_2$ ratios plotted against the $\Delta CO/\Delta ffCO_2$ ratios. The black dots show all our measured ratios from the single-height approach where we have CO as well as NO_x data available. Ratios classified as probably influenced by the industry emission sector (see figures 8 and 9 in the section discussing the temporal variability of in-situ measurements) are plotted in grey, and their error weighted mean is shown in orange.

The coloured markers represent emission ratios obtained from the TNO inventory for comparison. They are calculated for the three emission sectors industry (TNO sector A and B) in red, heating (sector C) in green and traffic in blue, which is further split into gasoline (F1), diesel



(F2) and a mix of all fuel types (F1-F4). Those ratios have been calculated by taking the ratio of the total emissions within a region of about 45 km x 35 km around the KIT tower (the area shown in figure 4). For the industry sector also the emissions of the point sources inside this region have been considered. For point sources with no reported CO, we used the reporting threshold value of 500 t/yr so that the obtained mean industry CO ratio has to be regarded as an upper limit value for the CO/ffCO₂ ratio. The uncertainties of the inventory-based emission ratios are provided by TNO [personal communication I. Super (2020)]. The uncertainties are based on a Monte Carlo simulation to estimate the CO₂, CO and NO_x emission uncertainty per aggregated source sector by perturbing the activity data and emissions factors using the German national inventory report's initial uncertainties.



Figure 12: ΔNO_x/ΔffCO₂ ratios plotted over ΔCO/ΔffCO₂ ratios. In black, the atmospheric in-situ ratios of the flask measurements are shown, in grey ratios influenced by the industry emission sector. The orange dot shows the error weighted mean of the industry influenced in-situ ratios. The coloured dots denote inventory-based emission ratios for the three sectors industry (red), traffic (blue) and heating (green) obtained from TNO for the year 2019 from a region of approximately 45 km x 35 km around the KIT tower. The averaged industry ratio is the mean of all sources from TNO sectors A and B, the traffic is further split into values for diesel, gasoline and the mix of all fuel types.

The majority of the atmospheric in-situ $\Delta proxy/\Delta ffCO_2$ ratios scatter in a triangle which is spanned at the vertices of the TNO emissions ratios for the three dominant source sectors. Two in-situ events result in negative proxy/ffCO₂ ratios exceeding their 1 σ uncertainty. The negative ratios are caused by spurious negative proxy enhancements due to a slightly higher background signal



in situations where generally no strong enhancement occurred. The individual events can be seen in appendix B and are assignable by their numbers.

For the industrially influenced samples (denoted by the grey points), we calculated the uncertainty weighted atmospheric mean proxy ratio for industrially dominated sources as $\Delta CO/\Delta ffCO_2 = 0.81\pm0.81$ ppb/ppm and $\Delta NO_x/\Delta ffCO_2 = 0.51\pm0.25$ ppb/ppm. This experimentally determined ratio of the industry sector agrees with the TNO emissions ratios within their uncertainties.

The remaining less industrially influenced event ratios scatter between the emission ratios for the three dominant source sectors. Thus, in theory, we can apply the three independent observables, $^{14}CO_2$, NO_x and CO to separate the ffCO₂ enhancements into the three main emission sectors. This can be achieved by exploiting the observed Δ ffCO₂, Δ NO_x and Δ CO enhancements combined with *known* proxy/ffCO₂ emission ratios (either from inventories or source sector-specific measurements, e.g., in D2.8) of the three respective source categories. We call this idea further on the multi-proxy approach.

Before applying the multi-proxy approach, we need to discuss its limitations and preconditions:

Independence of the observables

The ability of the multi-proxy approach for sectoral disaggregation depends on how well the source sectors can be separated in the CO/ffCO₂ and NO_x/ffCO₂ space. Based on the TNO emission ratios, we find a distinct separation of the three sectors for the KIT surroundings. Further research has to be done to determine the multi-proxy approach's disaggregation capacity, considering the uncertainty in the emission ratios and the observational uncertainties of the atmospheric ratios.

Chemical lifetime of the observable

While ¹⁴CO₂ and CO can be seen as stable tracers, this is not the case for NO_x. NO_x has a complex and variable chemical lifetime, which can vary between 6 h and 29 h, depending on, e.g., the NO_x concentration itself, OH-, VOC- and ozone concentrations and the availability of sunlight (Kenagyet et al., 2018; Shah et al., 2020). Thus, thorough modelling of the atmospheric NO_x chemistry is essential to derive quantitative source disaggregation. Chemical box-models like FOAM (Wolfe et al., 2016) could provide a first insight into the uncertainty in the disaggregation related to changing NO_x lifetimes.

Uncertainty and spatial heterogeneity of emission ratios

The uncertainty and the spatial heterogeneity of the emission ratios interfere with the independence and the uniqueness of the emission ratios for the individual sources. The heating sector is a good example of this problem. While, depending on the fuel type, different heating systems have largely different proxy/ffCO₂ ratios (see VERIFY deliverable report D2.8) this variability is averaged out by atmospheric mixing, if the different heating systems are homogeneously distributed. If, however, different heating systems dominate in different footprints, the atmospheric mixing fails, and footprint specific multi-proxy approaches would have to be applied.



4.6.3 Findings from the Total Column observations

In order to also generate a double-ratio plot for the total column observations showing $\Delta NO_{2,VCD}/\Delta XCO_2$ over $\Delta XCO/\Delta XCO_2$ both ratios are treated as being interdependent, which means that both ratios are required to achieve a R² > 0.5 in the fits, thereby requiring that on the resulting days both $\Delta NO_{2,VCD}$ and ΔXCO are correlated with ΔXCO_2 . Clear variability along both axes of the plot has to be observed above the level of significance. We discuss the observed range of variability below (in the section discussing the comparison of proxy/ffCO₂ ratios derived from in-situ and total column data). The individual events shown in Figure 13 are listed in Table 2. For testing the assumption whether the strongest events observed (which will be characterized in consequence by highest R² values) are plume observations of the hard-coal fired power plant introduced in the section, but no clear preferred direction is found as can be seen in Fig. 14. The number of events seems still too low for this kind of analysis. It would be required to continue the observation for several years in order to significantly increase the number of observed events.



Figure 13: Double ratio plot with the events found on the time-period constrained to the MAX-DOAS availability of data, July 2019 to November 2020.

Event correlative number used in figure 14	Date
1	2019-07-24



2	2020-01-16
3	2020-03-19
4	2020-04-02
5	2020-04-07
6	2020-04-08
7	2020-05-08
8	2020-09-15

Table 2: List of events detected by the remote-sensing technique



Figure 14: Remote-sensing events with $R^2 > 0.5$ classified by a correlative number. The colour represents individual R^2 values of the fits and the angular orientation in the polar plot is given by the averaged wind direction at noon time. No clear correlation between R^2 and direction becomes apparent.

5. Comparison of proxy/ffCO₂ ratios derived from in-situ and total column data



Directly comparing the in-situ and total column based proxy/ffCO₂ ratios is not possible, since the total column measurements cannot measure $ffCO_2$. The range of variation of the proxy/ffCO₂ ratios of both techniques, shown in the double ratio plots (figure 12 and figure 13) is clearly distinct. The total column ratio variations are reduced by a factor of 12 on the CO/ffCO₂ axis and by a factor of 2.5 on the NO_x/ffCO₂.

Thus, in figure 15 we adapted the in-situ measurements to show the same quantities as the total column observations do, e.g. NO₂ instead of NO_x and CO₂ instead of ffCO₂. In-situ and total column ratios for the same quantities are much more comparable in terms of variability although the insitu measurements, especially the CO/CO₂ variability, are still higher. Due to the fundamentally different meteorological conditions which are preferred for the in-situ and the total column measurements², there is only one common day for both observation strategies on April 7, 2020, shown by number 13 of the in-situ data and number 5 by total column. Though the in-situ signal sampled between 4:00 and 5:00, the in-situ and the total column observation even on that single common day do not actually sample the same event and are therefore unlikely to agree.

The replacement of ffCO₂ by CO₂ changed the in-situ ratios considerably. Thus, the main reason for the discrepancies between in-situ and total column seems to be successfully identified (the transition NOx to NO₂ is of smaller impact). We have to conclude, that the assumption of the short-term variability being superimposed on the total column signal is dominated by individual local, strong emitters (see section on temporal variations in the total column measurements), is generally not tenable. From the in-situ measurements, we could conclude that the short-term variability in the total column signal has a comparable fossil to non-fossil share as the in-situ signals themselves. However, this is not surprising as the in-situ measurements are exploiting the short-term variability of its signal as well. Thus, we conclude that for accurate source apportionment and comparison with inventories, an observational method pinning down the ffCO₂ share is required, which unfortunately cannot be achieved by current remote sensing technology.

² Large in-situ enhancements are observed during atmospheric situations with suppressed vertical mixing, while on the other hand total column observations work only with clear sky conditions which is often going along with enhanced atmospheric mixing





Figure 15: Double ratio plot, similar to figure 12, but zoomed-in and with ΔNO_2 instead of ΔNO_x and total ΔCO_2 instead of $\Delta ffCO_2$. Black and grey denotes in-situ measurements, light blue measurements obtained from the total column observations. The red marker represents the mean industry ratio from TNO inventory. Compared to figure 12, the in-situ ratio of number 11 is missing in this plot, since it shows a strongly negative $\Delta CO/\Delta CO_2$ ratio. This results from a slightly negative CO_2 enhancement, probably due to strong photosynthesis (see number 11 in appendix B).



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6. Conclusions

The main conclusions from the in-situ observations of our study are that for the industrial sector we found a mean $\Delta CO/\Delta ff CO_2$ ratio of 0.81±0.81 ppb/ppm along with a $\Delta NO_x/\Delta ff CO_2$ ratio of 0.51±0.25 ppb/ppm. Both ratios are within their uncertainties compatible with the TNO-predicted $proxy/ffCO_2$ emission ratios for the power and industry sectors (TNO sectors A & B) within the 45 km x 35 km domain around KIT station. Also the $\Delta proxy/\Delta ffCO_2$ ratios of the other, not primarily industrially influenced samples can, within their uncertainties, be explained by a linear mixture of the three main emission sectors traffic, residential heating and industry. We have, however, not been successful in detecting the temporal changes in the $\Delta proxy/\Delta ffCO_2$ ratios. The combination of CO, NO_x and ¹⁴CO₂ measurements provides three independent observables allowing us to in principle separate the ffCO₂ enhancement in the three main contributors: industry, traffic and residential heating. The next challenging step is to correctly account for the NO_x lifetime in this multi-proxy approach. Only once this is achieved, the multi-proxy approach can provide quantitative source sector separation. Atmospheric chemistry models and potentially auxiliary measurements of ozone and VOCs might be needed to develop this approach further. Until then the multi-proxy approach should be tested in urban settings where the variable NO_x lifetime is less of an issue as the time delay between emission and measurement is much shorter.

The main conclusion from the remote sensing study is that the approach of using $\Delta \text{proxy}/\Delta X\text{CO}_2$ correlations for exploiting space-borne observations of such proxies for inferring ffCO₂ emissions is complicated in a region similar to the study region due to the high level of unpredictable variability in these correlations. However, our results indicate that the proxy/ $\Delta X\text{CO}_2$ correlations of at least strong localized sources might be recoverable from high-resolution space-borne observations to some degree. For a reliable quantification of ffCO₂ emissions using space-borne observations, we expect that a synergistic approach is needed, which connects the space-borne observations of columnar abundances of proxies and co-observed temporal and spatial CO₂ variations with the spatially resolved proxy/ffCO₂ correlations of several co-emitted species and advanced assimilation techniques using high-resolution meteorological dispersion modelling.



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Appendix A: Corrections for ¹⁴CO₂ emissions from nuclear facilities

¹⁴CO₂ emissions from nuclear facilities are known to contribute significantly to the atmospheric ¹⁴CO₂ budget and alter ¹⁴C-based ffCO₂ estimates by masking a certain share of the ¹⁴C-based ffCO₂ (Levin et al., 2003; Graven and Gruber, 2012; Kuderer et al., 2018). For the flask samples taken at KIT, we estimated the nuclear ¹⁴CO₂ influence using STILT. The annual mean ¹⁴CO₂ emissions for all European nuclear facilities were taken from the European RAdioactive Discharges Database (RADD, https://europa.eu/radd/). The temporal variations of these ¹⁴CO₂ emissions are, however, not reported. Based on monthly emission data from one nuclear power plant close to Heidelberg taken from Kuderer et al. (2018) we deduce an average monthly root mean square deviation of 36% for the ¹⁴CO₂ emissions from the long-term mean. Individual months may, however, deviate by up to 135%. We calculated the nuclear Δ¹⁴CO_{2,nuc} contamination for KIT according to Eq. A1 based on reported annual emissions:

$$\Delta^{14} CO_{2,nuc} [\%_0] = \frac{0.97 \ Q_{14C} F}{X_{CO_2} \ M_C \ A_{ABS}} \cdot 1000$$
 (A1)

The factor 0.97 accounts for the ¹³C normalisation in the Δ -notation, Q_{14C} is the nuclear ¹⁴CO₂ emission in Bq/(m²s). The RADD database provides nuclear ¹⁴CO₂ emissions in Bq/a for each nuclear facility. We assign these point source emissions to 1 m² in order to convert point- to areal emissions to become compatible with the footprint concept. M_c is the molar mass of carbon, A_{ABS} = 0.226 Bq/gC the specific ¹⁴C standard activity defined in Stuiver and Polach (1977), F the modelled footprint sensitivity in ppm/(µmol/(m²s)) and X_{CO2} the CO₂ mole fraction in ppm. More details on the nuclear correction can be found in Kneuer (2020).



Appendix B: Time series of all flask samples shown in the double ratio plot



Figure B1: Similar plot as figure 5, the uppermost panel shows the continuous measurements of CO₂, followed by CO in the second panel, and then NO_x, wind speed and direction and radon measurements, each referring to the specifications given at the left axis. The colours denote the sampling heights as given in the legend. For detailed description of the plot please refer to the main text in the section on in-situ measurements. The number serves as identification for the ratios in the double ratio plots.

The following plots in appendix B are built by the same pattern.





Number 2, 2019-10-24 to 2019-10-25 $\Delta CO_2 = (19.23 \pm 0.07) \text{ ppm}, \Delta ffCO_2 = (7.50 \pm 1.01) \text{ ppm}, \Delta CO = (36.26 \pm 1.02) \text{ ppb}, \Delta NO_x = (6.22 \pm 0.13) \text{ ppb}$

















Number 6, 2019-12-17 to 2019-12-17















































Number 18, 2020-04-17 to 2020-04-17 $\Delta \text{CO}_2 = (13.34 \pm 0.03) \text{ ppm}, \text{ } \Delta \text{ffCO}_2 = (5.73 \pm 1.07) \text{ ppm}, \text{ } \Delta \text{CO} = (-6.33 \pm 2.09) \text{ ppb}, \text{ } \Delta \text{NO}_x = (5.64 \pm 0.15) \text{ ppb}$ $\Delta \text{CO}/\Delta \text{ffCO}_2 =$ -1.11 ±0.42, $\Delta \text{NO}_x/\Delta \text{ffCO}_2 =$ 0.99 ±0.19 $\Delta \mathrm{ffCO}_2 \; \begin{bmatrix} \mathrm{ppm} \end{bmatrix}$ 517 $\overset{^{\mathrm{cl}}}{\overset{\mathrm{M}}{\mathrm{O}}}$ $\overset{\mathrm{M}}{\overset{\mathrm{d}}{\mathrm{O}}}$ $\overset{\mathrm{d}}{\mathrm{d}}$ 417 CO [ppb] 200150NO $_x$, NO $_2$ [ppb] NO_{x} 50 NO_2 0 wind speed [m/s] 100 360 wind dir [°] 270180900 10 $^{214}\mathrm{Po}$ $[\mathrm{Bq}/\mathrm{m}^3]$ 503:00 06:00 09:00 12:00 15:00 18:00 21:00 time [hour] - 30m - 60m - 100m - 200m 📒 signal flask 200 m \equiv signal flask 30 m \equiv bg flask m emean flask m mean in-situ $-\Delta
m ffCO_2$



Number 19, 2020-04-17 to 2020-04-17 $\triangle CO_2 = (27.05\pm0.03) \text{ ppm}, \Delta ffCO_2 = (13.33\pm1.11) \text{ ppm}, \Delta CO = (35.08\pm2.56) \text{ ppb}, \Delta NO_x = (10.83\pm0.19) \text{ ppb}$









Appendix C: column-averaged CO₂, CO, NO₂ and wind direction (200 m level) for identified events

Graphic representation of the methods used for the delta calculation for each gas and for each found event. The description of the left and right panel is the same as Figure 6 and 7 respectively.























