



Evaluation of nine years of continuous $\delta^{13}\text{CO}_2$ measurements in Heidelberg, Germany

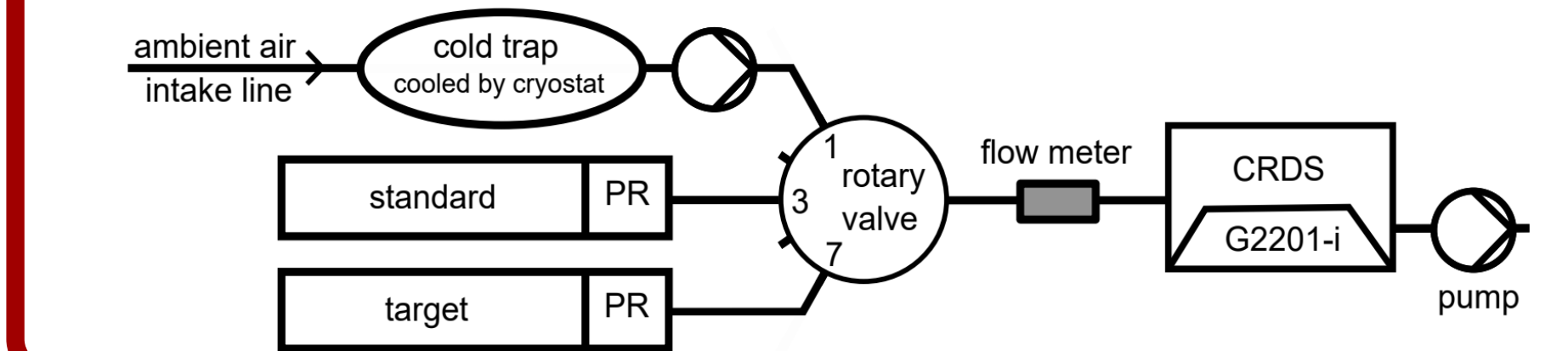
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Motivation

- Urban areas produce ~ 70 % of anthropogenic CO_2 emissions [1]
- Provide a basis for tracking the effectiveness of emission reduction policies

Laboratory Setup:

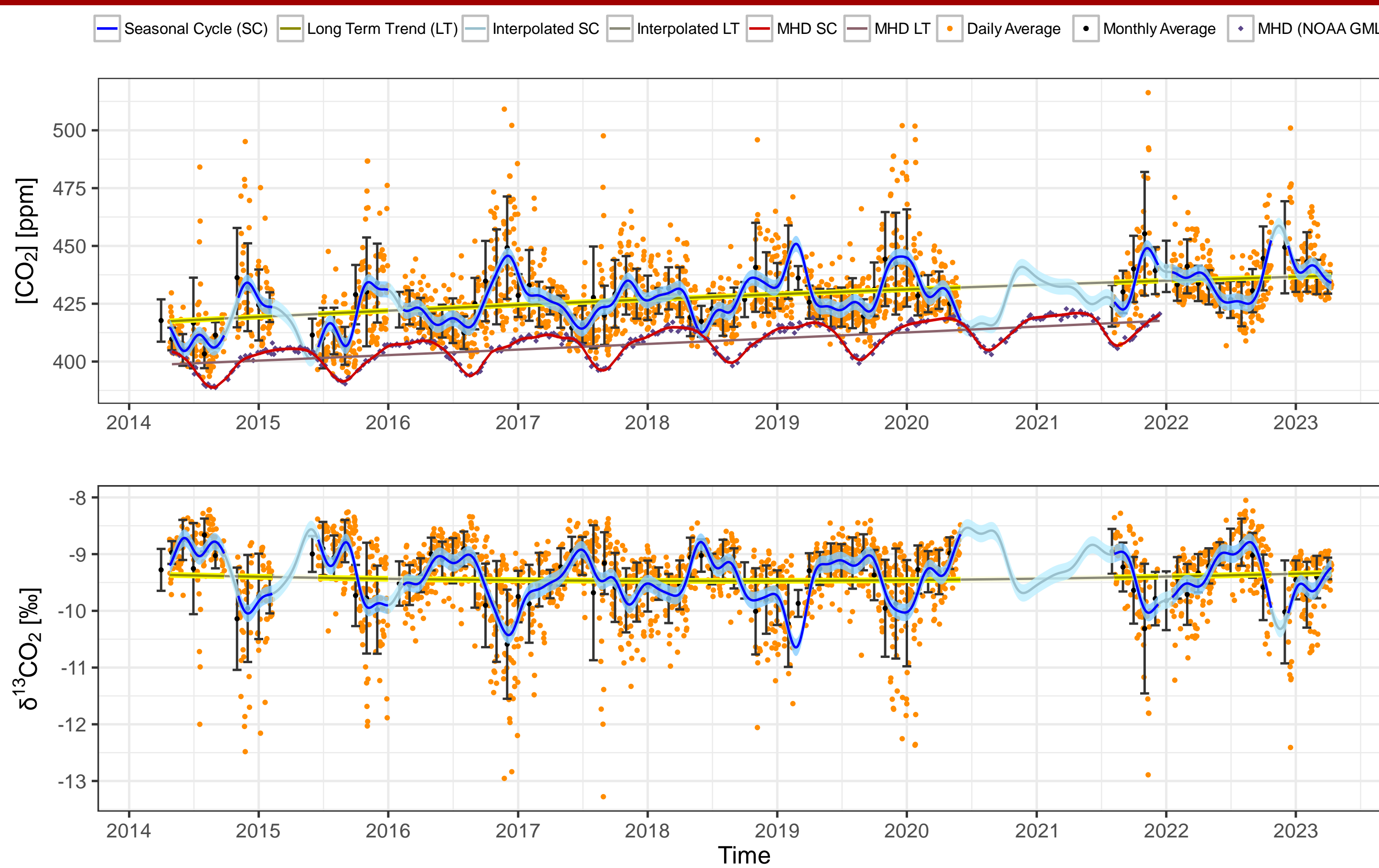


Ambient Air Measurements

- Continuous [$^{12}\text{CO}_2$] and [$^{13}\text{CO}_2$] measurements since 2014 from inlet 30 m above street level
- Cavity ring-down spectrometer (CRDS, Picarro model G2201-i) with drying system
- Single point calibration with interpolated values of known standards measured every 5 hours
- Calibration gases were analysed at MPI for Biogeochemistry in Jena for $\delta^{13}\text{CO}_2$ to link our measurements to the VPDB isotope scale
- Target mixtures measured to test long-term stability of measurements

Years Target in Use	Mean [CO_2] \pm SD [ppm]	Mean $\delta^{13}\text{CO}_2$ \pm SD [‰]
2014 - 2018	484.5 \pm 0.1	-11.0 \pm 0.1
2019 - 2020	381.7 \pm 0.1	-8.8 \pm 0.1
2021 - 2023	366.42 \pm 0.08	-8.7 \pm 0.2

Nine Year Time Series



- Daily and monthly means of minutely values shown
- [CO_2] background values from Mace Head (MHD) station, Ireland shown alongside for comparison [3]
- Seasonal [CO_2] cycle similar to and slightly ahead of background cycle
- $\delta^{13}\text{CO}_2$ values relative to VPDB scale
- $\delta^{13}\text{CO}_2$ and [CO_2] are quite strongly anticorrelated (Pearson's $R^2 = 0.89$)
- Significant increase of $2.32 \pm 0.03 \text{ ppm yr}^{-1}$ for [CO_2]
- No significant overall trend for $\delta^{13}\text{CO}_2$

Moving Keeling/Miller-Tans Plot Method

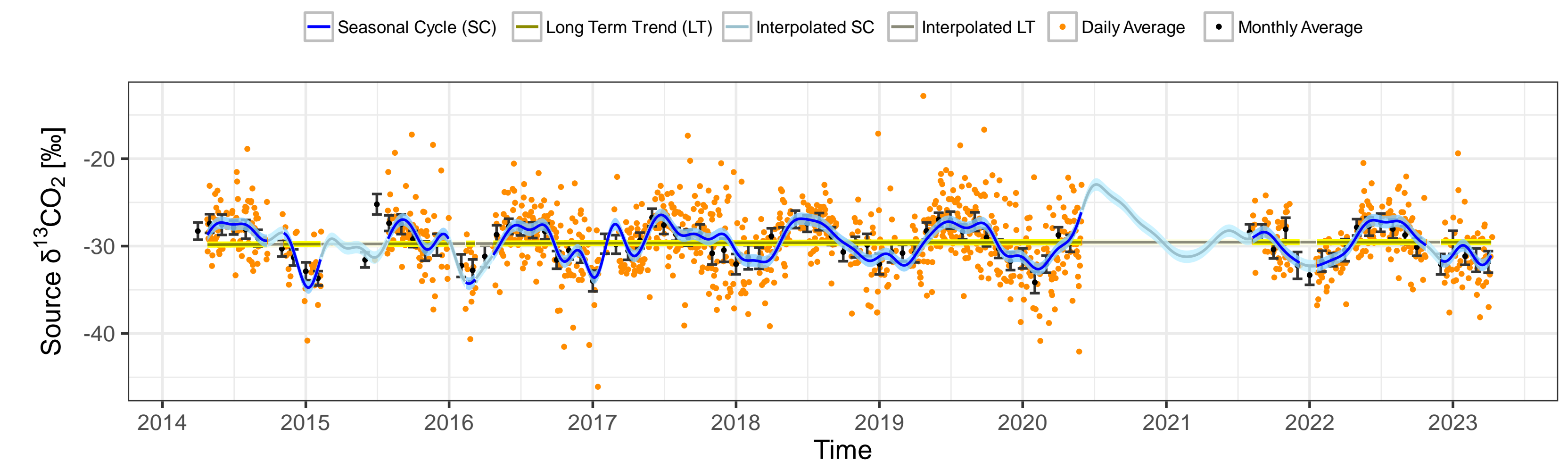
$$R^{13} = \frac{[^{13}\text{CO}_2]}{[^{12}\text{CO}_2]}, \delta c = \left(\frac{R_{\text{sample}}}{R_{\text{VPDB}}} - 1 \right) \cdot 1000 \text{‰}$$

$$c_{\text{obs}} = c_{\text{bg}} + c_s, c = [\text{CO}_2]$$

$$\delta c_{\text{obs}} \cdot c_{\text{obs}} = \delta c_{\text{bg}} \cdot c_{\text{bg}} + \delta c_s \cdot c_s$$

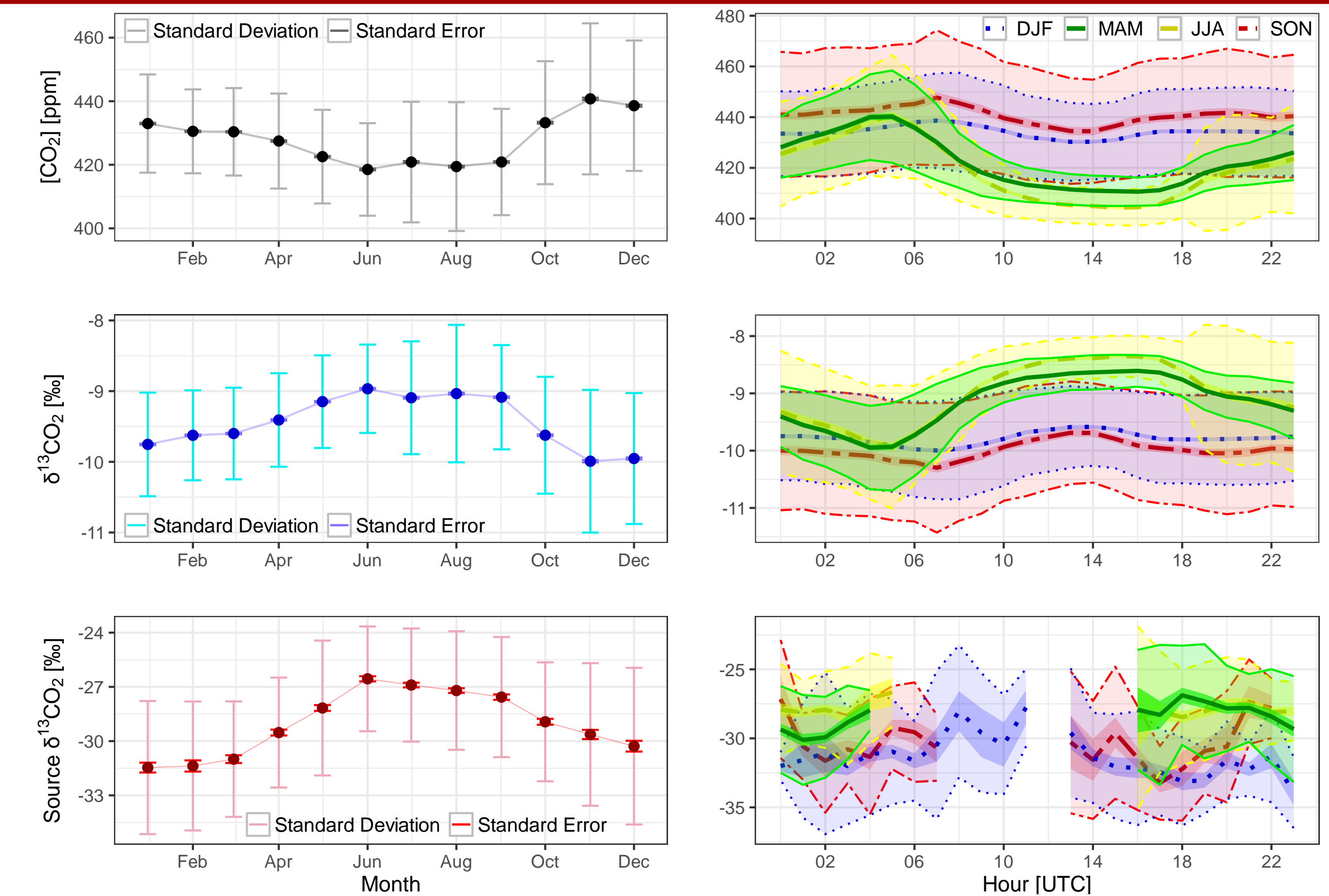
$$\delta c_{\text{obs}} \cdot c_{\text{obs}} = \delta c_s \cdot c_{\text{obs}} + c_{\text{bg}} (\delta c_{\text{bg}} - \delta c_s)$$

- 5 hour moving windows, using hour-averaged values
- Filter Conditions [4]:
 - $\Rightarrow \geq 5 \text{ ppm } [\text{CO}_2]$ total increase
 - \Rightarrow Monotonous [CO_2] increase
 - $\Rightarrow < 2 \text{‰}$ uncertainty in Miller-Tans Slope
 - \Rightarrow Reduced $\chi^2 < 10$; $R^2 > 0.75$

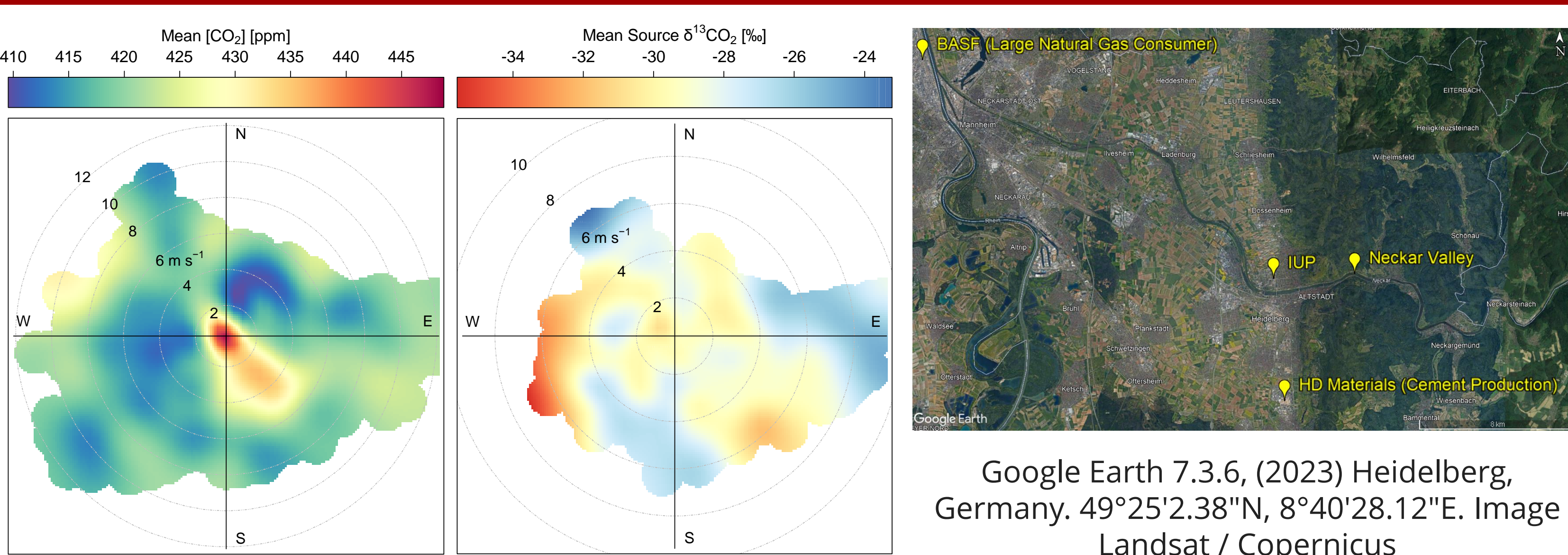


Seasonal and Daily Cycles

- Long term trend subtracted and mean values added to calculate the annual and diurnal cycles
- Significant annual cycles for [CO_2], $\delta^{13}\text{CO}_2$, and the source $\delta^{13}\text{CO}_2$
- Significant diurnal cycles for [CO_2] and $\delta^{13}\text{CO}_2$ for all seasons
- Amplitude of [CO_2] and $\delta^{13}\text{CO}_2$ diurnal cycles greatest in summer
- Limited daytime source $\delta^{13}\text{CO}_2$ values due to daytime CO_2 sink
- More source $\delta^{13}\text{CO}_2$ values obtained in summer and spring due to stronger [CO_2] diurnal cycle



Comparison with Wind Direction and Wind Speed



- CRDS located at Institute for Environmental Physics (IUP)
- Strong easterlies from Neckar Valley
- Enriched Isotope values likely from HD Materials
- Depleted values likely from natural gas combustion

Outlook and Next Steps

- Collaborate with CO_2 modellers to better identify contributions from local sources
- Compare with local and regional emission estimates to test their accuracy
- Use as a baseline to check the effectiveness of emission reduction policies

References and Acknowledgements

- [1] IEA (2021), Empowering Cities for a Net Zero Future, IEA, Paris <https://www.iea.org/reports/empowering-cities-for-a-net-zero-future>, License: CC BY 4.0
- [2] Hoheisel A. (2021), Evaluation of greenhouse gas time series to characterise local and regional emissions, PhD Dissertation, Institute Environmental Physics, Heidelberg University
- [3] Lan, X., E.J. Dlugokencky, et al. (2022), Atmospheric Carbon Dioxide Dry Air Mole Fractions from the NOAA GML Carbon Cycle Cooperative Global Air Sampling Network, 1968-2021, Version: 2022-11-21, <https://doi.org/10.15138/wkgj-f215>
- [4] Vardag, S. N., et al. (2016) Evaluation of 4 years of continuous $\delta^{13}\text{C}(\text{CO}_2)$ data using a moving Keeling plot method, Biogeosciences, 13, 4237–4251, <https://doi.org/10.5194/bg-13-4237-2016>

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