Extending capabilities in atmospheric monitoring of methane stable isotope ratios

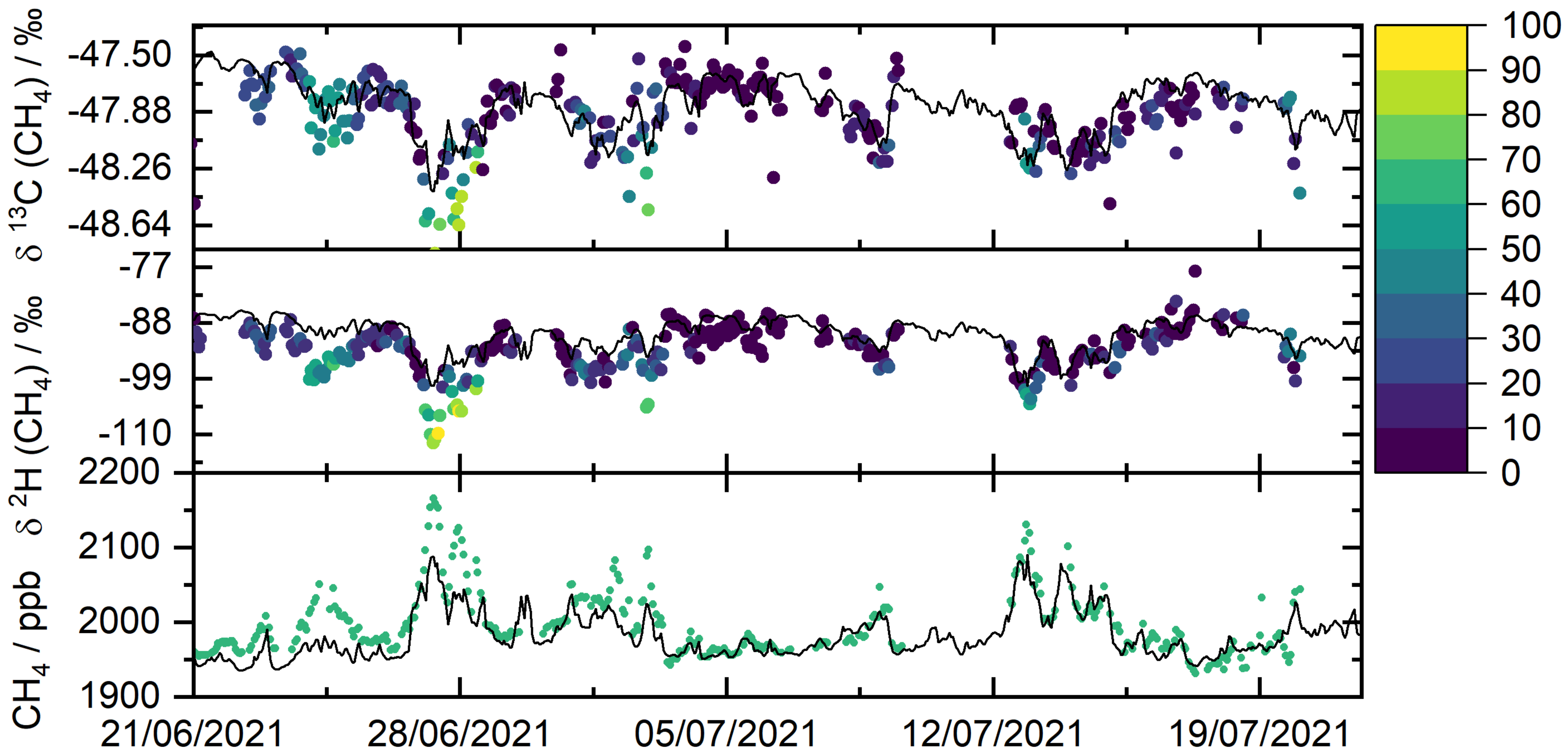
Tim Arnold[1,2], Ed Chung[1,2], Chris Rennick[1], Emmal Safi[1], Alice Drinkwater[2,1], Caroline Dylag[1], Sara Defratyka[2,1], Volker Ebert[3] and Javis Nwaboh[3]

1 National Physical Laboratory, Teddington, UK
2 School of Geosciences, University of Edinburgh, Edinburgh, UK
3 Physikalisch-Technische Bundesanstalt (PTB), 38116 Braunschweig, Germany

tim.arnold@npl.co.uk

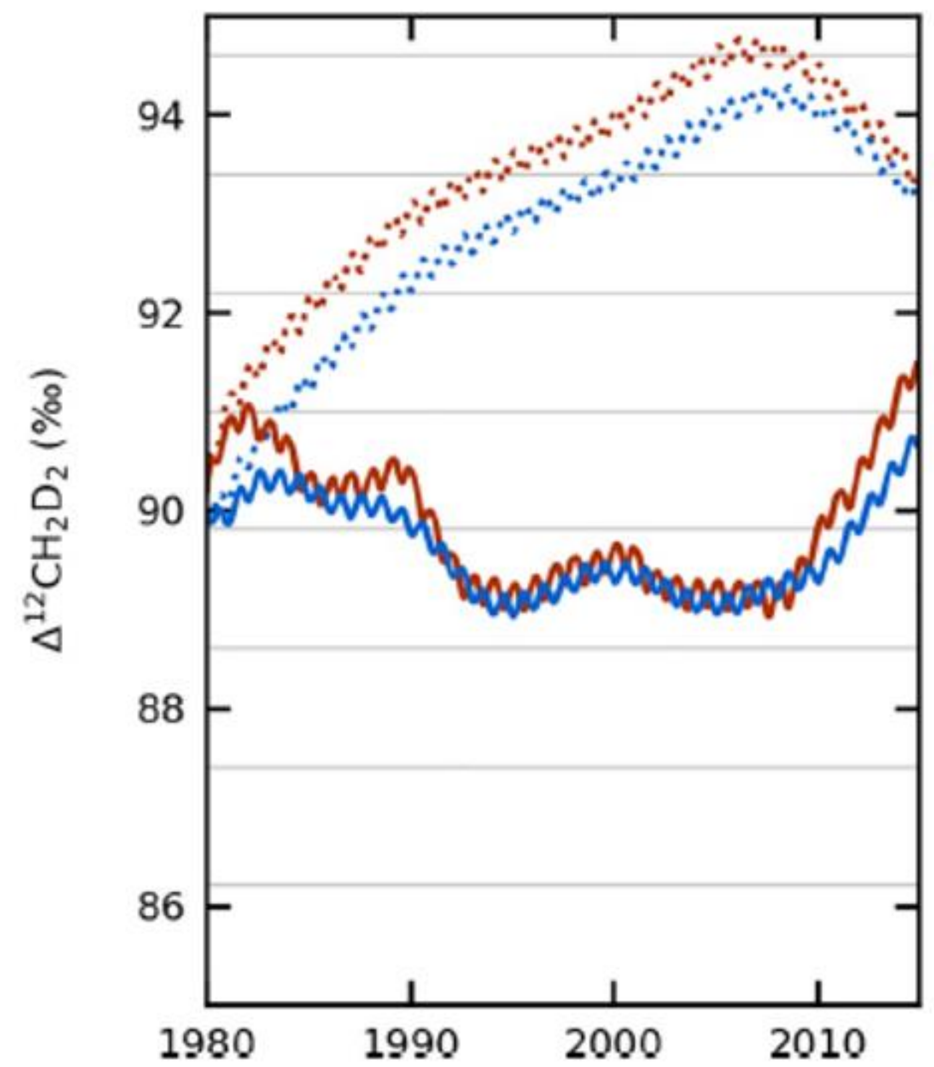
1. Developing methods for in situ monitoring

At regional scales the difficulty in making high-quality continuous measurements of the singly-substituted isotopologues hampers the routine take up of isotope ratios in emissions estimation frameworks. In Rennick et al. (2021) we show a new way to measure $\delta^{13}C(CH_4)$, $\delta^{2}H(CH_4)$ and CH_4 amount fraction simultaneously in ambient air samples using a laser spectrometer system. Importantly we develop a calibration protocol based on a combination of synthetic and ambient air compressed gaseous reference materials, which maximises performance in terms of accuracy and precision (see Theme 2 A7 presentation by Chris Rennick). In 2021 the system was deployed to a tall tower monitoring site in the UK (a GAW regional station) to assess the utility of continuous isotope ratio measurements for country-scale emissions verification. *The figure below demonstrates one month of measurements from this deployment together with model estimates using output from the NAME particle dispersion model (courtesy of the Met Office), available data for source signatures (taken from Sherwood et al., 2021) and inventory-based ('bottom-up') emissions estimates.*



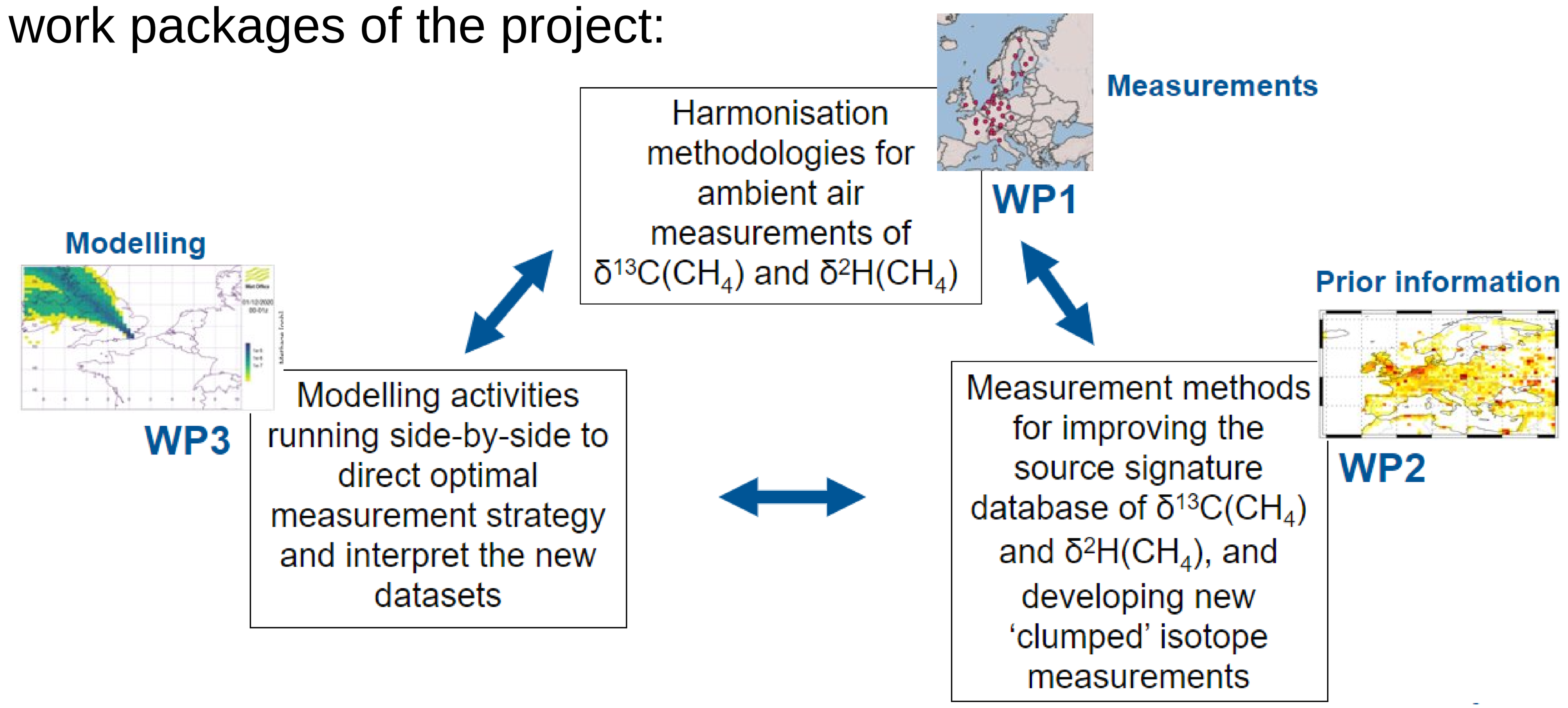
2. Delving deeper with rare stable isotopologue ratios

Trends in global atmospheric CH_4 – both mixing ratios and isotope ratios – are explained by various flux scenarios, from tropical wetland emission increases through to reductions in global hydroxyl. Looking beyond the singly-substituted isotopologues in Chung and Arnold (2021) we modelled the potential of the doubly-substituted isotopologues (isotopologues containing two or more rare-isotope substitutions) to contribute to understanding the longer-term global atmospheric CH_4 cycle. *The figure on the right shows that under slightly different global flux scenarios differences in the ratio $^{12}CH_2D_2/^{12}CH_4$ would result that would be greater than attainable measurement precision.* We await if these modelled estimates reflect the atmosphere ready play a role in global methane flux estimation.



3. Metrology for European emissions verification on methane isotopes: isoMET

isoMET, the 3-year European Metrology project funded by Euramet from October 2022 will look to develop the infrastructure necessary to bring methane isotope ratios routinely into top down emissions reporting and develop early the metrology of doubly-substituted isotopologue measurements. This requires work in three areas, which are set out within the three work packages of the project:



References: Sherwood, O. A., et al., Global Inventory of Fossil and Non-fossil δ13C-CH4 Source Signature Measurements for Improved Atmospheric Modeling, 2020; Rennick et al., Boreas: A Sample Preparation-Coupled Laser Spectrometer System for Simultaneous High-Precision In Situ Analysis of δ13 C and δ2H from Ambient Air Methane, 2021 ; Chung and Arnold, Potential of Clumped Isotopes in Constraining the Global Atmospheric Methane Budget, 2021