Preconcentraton of Atmospheric Methane for High-Frequency Isotopic Measurement

Christopher Rennick (1), Tim Arnold (1,2), Francesco Bausi (1), Joshua Schofield (1), Edward Chung (1), Alistair Manning (3), Kieran Stanley (4), and Simon O'Doherty (4)

(1) National Physical Laboratory, Emissions and Atmospheric Metrology, Teddington, United Kingdom (chris.rennick@npl.co.uk), (2) School of GeoSciences, University of Edinburgh, Edinburgh, UK, (3) Met Office, Exeter, UK, (4) Atmospheric Chemistry Research Group, School of Chemistry, University of Bristol, Bristol, UK

The mixing ratio of methane (CH_4) in the atmosphere has more than doubled over the past 150 years with significantly varying growth rates over this period. The reason for this variable growth is not clear, owing to diverse and changing sources – such as wetlands, landfill, agriculture or fossil fuels – and possible changing magnitudes in the sinks – largely the reaction with OH.

We have constructed a field-deployable cryogenic preconcentration system that extracts a CH_4 sample from a large volume of ambient air and delivers it to a diode laser spectrometer (Aerodyne TILDAS) for simultaneous measurement of δ-^{13}C and δ-D. Initial testing shows that this system is capable of continuous, automated measurements at a precision approaching that of off-line mass spectrometric analysis. We also quantify the influence of mixing ratio and matrix gas on the spectroscopic lineshape and the resulting systematic error in δ-^{13}C and δ-D estimates.

Different sources emit CH4 with characteristic δ-13C and δ-D signatures. In order to understand the potential of isotope ratio measurements as a source tracer to verify the UK's sector specific emissions of CH_4, we simulate the isotopic variation at four UK greenhouse gas tall-tower sampling sites based on emission maps from the National Atmospheric Emissions Inventory and output from the Numerical Atmospheric-dispersion Modelling Environment (NAME). These simulations show the level of precision required to detect variations of up to -0.5‰ for δ-^{13}C and -10‰ for δ-D relative to the background values due to mixing of emissions from the three major UK sources: waste, agriculture and energy infrastructure. Further analytical developments of the system are in progress to reach and exceed these requirements, with planned deployment to a UK tall tower site in 2019.