Novel stable isotopic measurements for understanding atmospheric methane

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We demonstrate the possibilities for continuous high precision in situ measurements of $\delta^{13}$C(CH₄) and $\delta^{2}$H(CH₄) for understanding regional CH₄ emissions and explain how advances in nascent measurement techniques looking at ‘clumped’ CH₄ might improve our understanding on the global scale.

‘Boreas’ is a new fully automated sample-preparation coupled dual laser spectrometer system developed at the National Physical Laboratory, able to make accurate and precise simultaneous measurements of $\delta^{13}$C(CH₄) and $\delta^{2}$H(CH₄) through the measurement of isotopologue ratios of CH₄. Average daily repeatabilities of <0.08 ‰ for $\delta^{13}$C (n=10, 1 SD) and <1‰ $\delta^{2}$H of a compressed ‘background’ air sample (1.9 ppm dry air amount fraction CH₄) are achieved, making the measurements comparable to bulk isotope ratio mass spectrometry. These measurements are interspersed with air sample measurements from the roof of our building in west London, and we show the possibility to differentiate potential sources of CH₄ under different meteorological conditions.

We use a particle dispersion model (the Met Office’s NAME) and inverse method to predict the possible impact of the new continuous isotope ratios measurements on quantification of emissions from individual source sectors, should the technique be deployed to a tall tower network of monitoring sites in the UK.

Finally, our theoretical analysis is extended beyond the most abundant isotopologues of CH₄ to look at how analysis of the clumped isotopes might be able to impact our understanding of interannual variability in the global CH₄ burden. We incorporate measurements from emission sources and information on reaction rates into a global box model (with an inverse method) to show the added value of strategic ∆CH₂D₂ and ∆¹³CH₃D ambient air measurements relative to bulk isotope ratios alone.