

# CLIMATE CHANGE TO THE NUCLEAR FUEL CYCLE: EXPANDING THE $^{14}\text{CO}_2$ DATABASE FOR NON-AMS FIELD MEASUREMENT SYSTEMS

Bruno D.V. Marino, David E. Tolliver, Robert G. O'Donnell  
Planetary Emissions Management Inc., 711 Atlantic Ave. Boston, MA



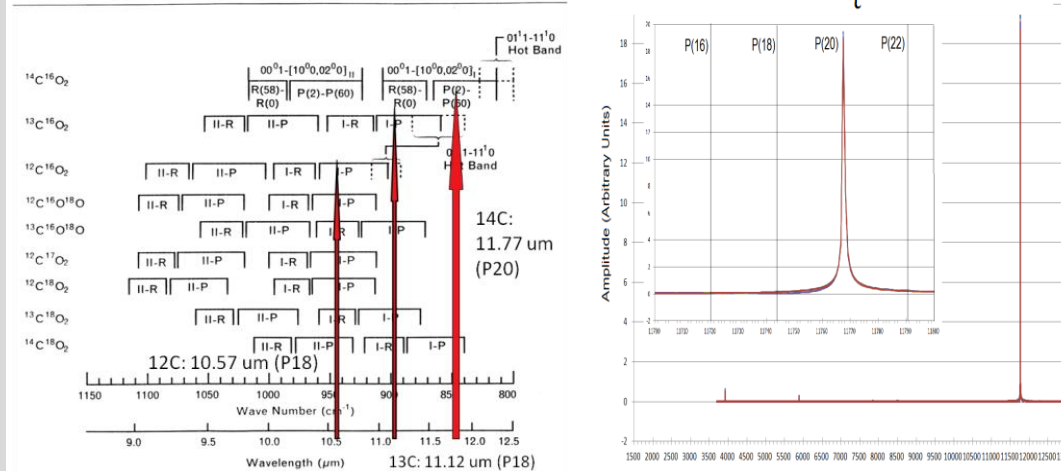
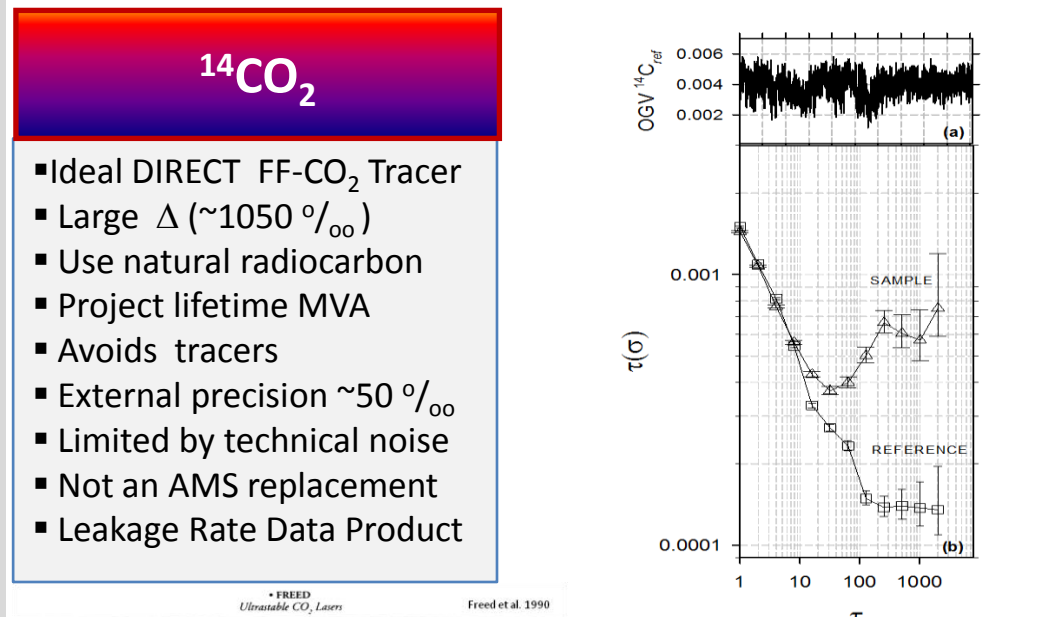
## Abstract

Accelerator Mass Spectrometry is well known and universally employed for radiocarbon analysis but is not adaptable to field measurements limiting applications.  $^{14}\text{CO}_2$  is a key tracer for fossil fuel  $\text{CO}_2$  as well as for release of enriched  $^{14}\text{CO}_2$  characteristic of the nuclear fuel cycle with  $\text{D}^{14}\text{CO}_2$  values ranging from -1000 to  $\sim +500$  per mil. However, to exploit the full value of in situ  $^{14}\text{CO}_2$  data in diverse climate change and nuclear fuel cycle applications high data rate temporal and spatial field measurement systems are required. The development of non-AMS methods based on quantum cascade laser, cavity ring down and optogalvanic spectroscopy are emerging applications but not fully developed for field use or widely accepted. Spectral data for lasing transitions for  $^{14}\text{CO}_2$  are lacking in contrast to HITRAN data available for  $^{12}\text{CO}_2$  (626) and  $^{13}\text{CO}_2$  (636) (among other isotopologues 628, 638, etc.) in the spectral databases limiting development and innovation in non-AMS  $^{14}\text{CO}_2$  analytical systems. We review the corpus of  $^{14}\text{CO}_2$  spectral data spectral data available in the literature and document grating tuned isotopic lasers (e.g., Freed 1990; Bradley et al., 1986) well suited for expanded spectral studies of  $^{14}\text{CO}_2$  and inclusion in the HITRAN database. Available isotopic lasers for  $^{14}\text{CO}_2$  collaborative studies are described.

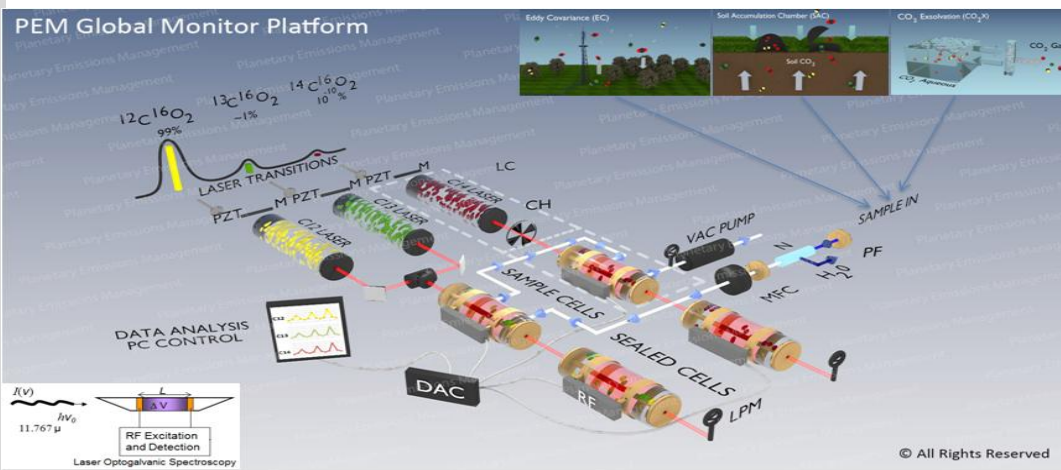
## Objectives

- Expand spectral database for  $^{14}\text{CO}_2$
- Integrate spectral data with new non-AMS field analyzers
- Develop laboratory for  $^{14}\text{CO}_2$  spectroscopy
- Collaborative instrument development
- Field testing of applications for fossil fuel & nuclear  $\text{CO}_2$  emissions quantification

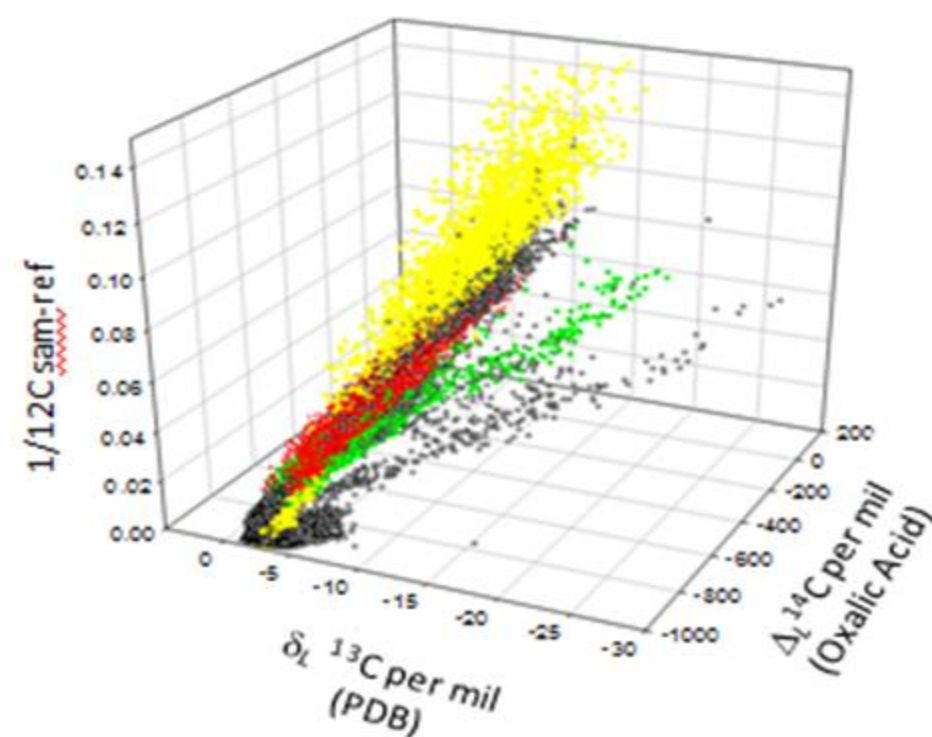
## Status



Marino, ms in preparation



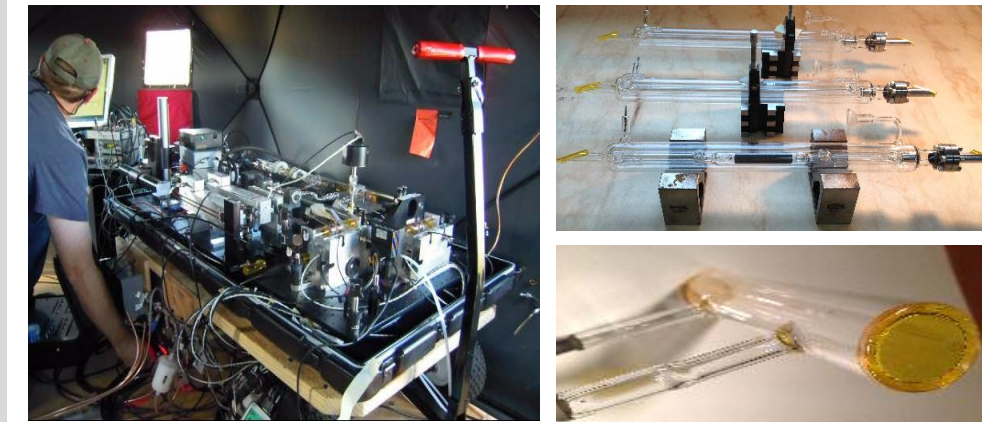
## CCUS Leakage MVA



Eddy Covariance Results, Soda Springs, ID  
Marino, ms in preparation

## $^{14}\text{CO}_2$ Gas Lasers

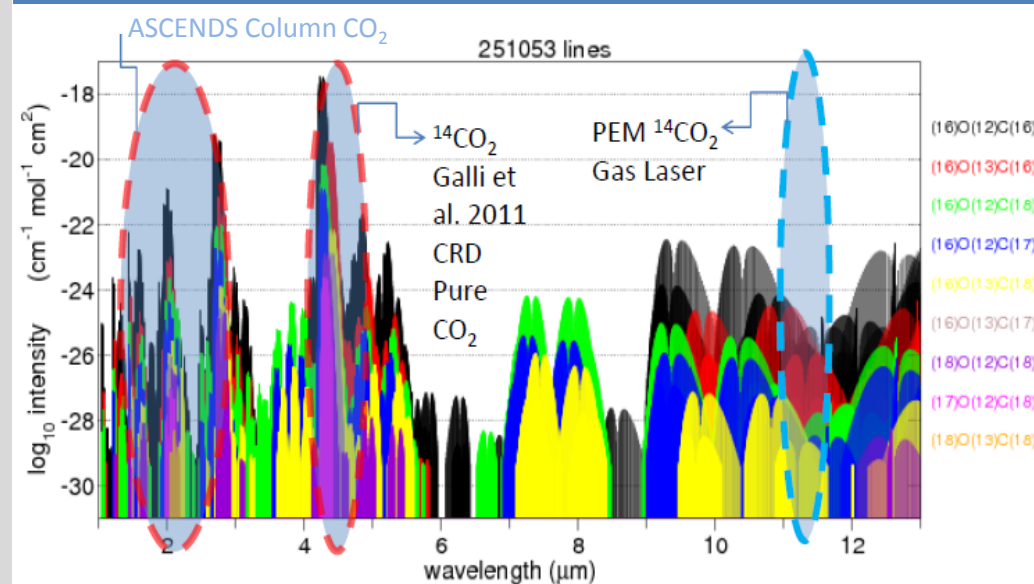
Free running and grating tuned  $^{14}\text{CO}_2$  lasers available for development research



PEM is establishing a  $^{14}\text{CO}_2$  spectroscopy laboratory using modular lasers developed by Charles Freed and colleagues of MIT LL



## $^{14}\text{CO}_2$ Spectroscopy



### NON-AMS FIELD READY $^{14}\text{CO}_2$ ANALYZER

**Methods**  
Laser Optogalvanic Spectroscopy (LOGS D<sub>1</sub>), ICLAS

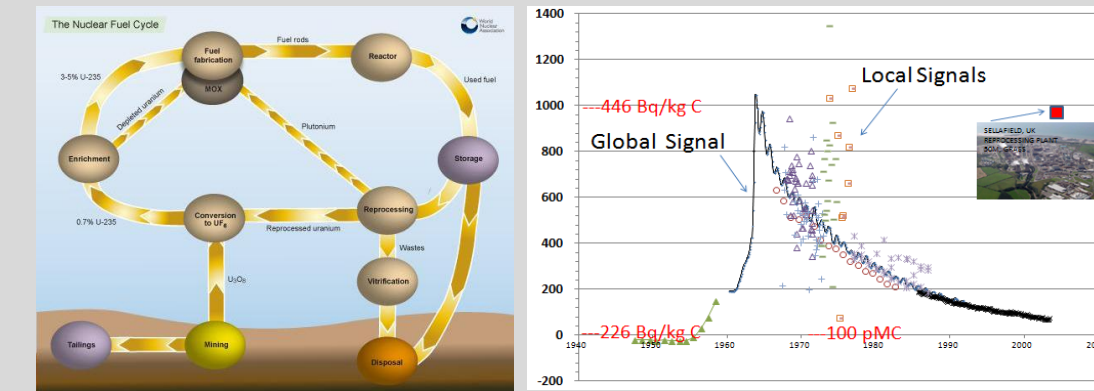
**Implementation**  
Murnick et al. 2008

**Requirements**  
Narrowband  $^{14}\text{CO}_2$  Laser, Intracavity, High Sensitivity Detection Cell, Standard Reference Cells, Calibration Routines, Integration with Diverse Field Instruments

**Status**  
Field Deployment Demonstrated (4 Sites), Integration with Soil, EC, Exsolvation Instrumentation, 14C Internal Precision ( $\sim 2$  per mil), 14C External Precision ( $\sim 50$  per mil)

**Problems**  
Resetability & External Precision, OGE Cell Noise, Component Upgrades, 14C Laser Fabrication, Persson et al. 2013  
Kinetic OGE-C isotopologue model lacking

## Nuclear Fuel Cycle



### Twin Perils: Energy & Climate Change

- Proliferation Risk Increases (undeclared/denied)
- Challenge for IAEA Global Detection & Monitoring
- Expanded Safeguards Needed
- NFC MVA on Local-to-Global Scales
- Improved Field Analyzers (e.g., QCL) Needed

## $^{14}\text{CO}_2$ Collaboration

- QCL, CRD laser fabrication
- Expansion of line positions, strengths
- Spectroscopy for field systems
- Testing evaluation of systems
- Satellite sensor systems
- Fossil-fuel emissions
- Nuclear fuel cycle emissions
- Integrated instrumentation platforms
- Landscape scale sensor networks
- Commercialization

## References/Contacts

- Bruno D.V. Marino, bruno.marino@pem-carbon.com
- David. E. Tolliver, detolliver@icloud.com
- Freed, C., 1990. Ultrastable  $\text{CO}_2$  Lasers. *The Lincoln Laboratory Journal*, 3(3), pp.480–496.
- Freed, C., Bradley, L. & O'Donnell, R., 1980. Absolute frequencies of lasing transitions in seven  $\text{CO}_2$  isotopic species. *IEEE Journal of Quantum Electronics*, 16(11), pp.1195–1206.
- Marino, B.D.V., 2014. Near Surface Leakage Monitoring for the Verification and Accounting of Geologic Carbon Sequestration Using a Field Ready 14C Isotopic Analyzer. OSTI ID: 1130969. DOE Contract #: FE0001116. Technical Report. 2014-04-14.
- Marino, B.D.V., Michelle Bright, and Glen Groninger., 2011. "Design and package of a  $^{14}\text{CO}_2$  field analyzer: the Global Monitor Platform (GMP)." *SPIE Optical Engineering+ Applications*. International Society for Optics and Photonics.
- Murnick, D.E., Dogru, O. & Ilkmen, E., 2008. Intracavity optogalvanic spectroscopy. An analytical technique for 14C analysis with subattomole sensitivity. *Analytical chemistry*, 80(13), pp.4820–4.
- Persson, A. et al., 2013. Evaluation of intracavity optogalvanic spectroscopy for radiocarbon measurements. *Analytical chemistry*, 85(14), pp.6790–8.