# Near Surface Leakage Monitoring for the Verification and Accounting of Geologic Carbon Sequestration Using a Field Ready $^{14}C$ Isotopic Analyzer

**FINAL TECHNICAL REPORT**

**Reporting Period Start Date: January 15,2010**

**Reporting Period End Date: January 14, 2014**

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**Report Date: April 16, 2014**

**DE-FE0001116**

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## 1.0 Abstract

Results for the development of a field ready multi-isotopic analyzer for $^{12}CO_2$, $^{13}CO_2$ and $^{14}CO_2$ and applications for carbon capture and storage (CCS) containment performance are described. A design goal of the field platform was to provide isotopic data with a high data rate, a standardized reference baseline and acceptable precision (e.g., ~ ±50 per mil $D^{14}CO_2$) for detection and quantification of fossil-fuel $CO_2$ CCS leakage scenarios. The instrument platform was not designed to replace high precision accelerator mass spectrometry. An additional goal was to combine project scale isotopic data and associated fluxes with unique financial instruments linking CCS containment performance to a publicly traded security providing project revenue to stakeholders. While the primary goals of the project were attained additional work is needed for the instrument platform and deployment within a full scale CCS site that was not available during the project timeframe.

**2.0 Table of Contents**

**3.0 Executive Summary**

The importance of carbon capture and storage (CCS) and related approaches designed to avoid carbon emissions from fossil fuel based power plants (e.g., carbon capture storage and utilization (CCUS) and enhanced oil recovery (EOR)) is incontrovertible (e.g., Bielicki et al. 2014). However, the transition of demonstration projects to fully functional commercial installations, a requirement for effective energy-sector GHG management, has lagged relative to projections and need for timely action (e.g., Watson et al. 2014). The lack of commercial CCS capacity can be seen as a "lagging indicator" of the energy industry as a whole in response to macro- economic factors (e.g., cost of energy), technology implementation for capture/injection and post-injection maintenance costs for captured $CO_2$ and equivocal public support for CCS approaches based on environmental health and safety issues (EHS) and incremental costs of CCS passed on to utility customers. The CCS value proposition for stakeholders is that high CCS performance (e.g., cost-effective capture and injection and long term, 100 year, >99%, containment) will result in atmospheric management of $CO_2$ emissions while providing economic benefits based on some form of carbon trading (e.g., Renner 2014). The lag in US CCS commercial installations has impeded exploration of the CCS full value proposition over the long-term including potential economic value to capital markets (e.g., public and private GHG trading participants) for high performance CCS projects. Deployment of long term CCS leakage detection systems such as proposed in the work performed was not attractive or feasible for early stage CCS demonstration projects available during this project timeline.

The results described here address the technological and financial requirements to realize the full value proposition for CCS cross-cutting temporal, spatial and financial dimensions of CCS. The development of a real-time, continuous-flow unique field analyzer, the Global Monitor Platform (GMP), for $^{14}CO_2$ (the only direct tracer for fossil fuel $CO_2$) to detect and quantify leakage of CCS $CO_2$ in the free atmosphere, soil gas and in the aqueous phase, coupled with a leakage-rate data product provides a performance linked financial instrument addressing economic, EHS and public support concerns for CCS. However, due to the lack of full-scale CCS sites during the project period, deployment of the PEM technologies was not transferred to a functioning CCS facility. However, fundamental advancements in the underlying field instrumentation, measurement protocols, experience at four field sites and theoretical application of CCS leakage data to unique CCS financial instruments were addressed and summarized herein. Detailed results will be available in pending peer reviewed publications.

The key results are as follows:

- A multi-isotopic field-ready analyzer, the Global Monitor Platform (GMP) for $^{12}CO_2$, $^{13}CO_2$ and $^{14}CO_2$ was fabricated, tested and deployed in the field at four unique field sites (e.g., Marino et al. 2011). This was the first demonstration of a multi-isotopic analyzer in the field. Remote operation with battery power was also demonstrated.
    - The technical basis for high sensitivity $^{14}CO_2$ instrument detection requires further experimentation and validation. The basis of the initial $^{14}CO_2$ laser and optogalvanic detector design (e.g., Murnick et al. 2008) was modified in 2011 in conjunction with a project team at the Kansas City Plant (KCP), Kansas City, MO. Subsequent work (e.g., Persson et al. 2013) confirmed uncertainties of the Murnick et al. (2008) system. The PEM GMP system developed by PEM and KCP differed significantly from and not directly comparable with existing systems (e.g., Murnick et al. 2008; Persson et al. 2013). The primary differences include: 1) non-saturating concentrations of sample $CO_2$, 2) low-power laser emission profile, 3) continuous-flow analysis, 4) free-running laser operation, 5) high pressure sample cell operation, 6) modulation frequency optimized for signal enhancement, 7) use of matched sealed reference cells with synchronous data acquisition for all isotopic species, and, 8) use of correction factors based on sealed reference cell responses to correct for non-resonant interactions. The goal of this work was not to replace high precision accelerator mass spectrometry (AMS) but to augment AMS approaches

to CCS $^{14}CO_2$ monitoring verification and accounting given the logistical and cost constraints of AMS.

- A precision of ± 50 per mil and ± 0.2 per mil was attained for GMP $\Delta^{14}CO_2$ and $\delta^{13}CO_2$, respectively, providing a new field capability for CCS leakage detection.
- Considerable improvements in both $\Delta\ ^{14}CO_2$ and $\delta\ ^{13}CO_2$ precisions are expected with readily achievable, low cost incremental upgrades for the GMP.

- The fabrication process and instrument integration for gas-filled $^{14}CO_2$ lasers and sealed reference cells were realized providing the basis for commercial production of a $^{14}CO_2$ laser and matched reference cells, critical components of a field-ready analyzer. $^{14}CO_2$ lasers were not readily available from commercial vendors.
- A field optical-table was fabricated and tested for integration of three narrow band lasers ($^{12}CO_2$, $^{13}CO_2$ and $^{14}CO_2$) with matched sample and reference cells, electronics and software control.
- The demonstration of stability and functionality of sealed reference cells inter-calibrated with NOAA reference gases and matched to sample cells provides the basis for networks of field analyzers ensuring comparability of data across analyzer locations within single and multiple CCS project locations.
- The GMP was integrated with commercial instruments including an eddy covariance system (provided by Lawrence Berkeley Laboratory), soil accumulation chambers ( LI-8100 and LI-8150 Multiplexer, LICOR Inc.) and an automated $CO_2$ exsolvation analyzer (GHG Sentinel, Axys Technologies Inc.) at four field sites.
- The GMP was deployed at two $CO_2$ analog sites (Mammoth Mountain, CA; Soda Springs, ID) and two city locations (Boston, MA; Indianapolis, IN) resulting in a range of emissions detection scenarios.
- A software program was designed and tested to acquire raw data, apply filtering routines and to provide comprehensive data characterization and calculations resulting in delta isotope ratios in the field.
- A web-based dashboard facility for access to GMP data at a given location was designed with flexibility for integration of external related CCS data including the full spectrum of vadose zone, bore-hole and seismic data.
- The requirements for and the design of a unique CCS financial instrument, based on PEM proprietary technology, was addressed theoretically providing for performance based CCS value in a publicly traded stock. The unique CCS financial instrument offers global access and participation of stakeholders for a given project or group of projects resulting in project revenue to offset CCS costs, provide for a "trust-fund" in case of CCS damage and a transparent, market driven regulator of EHS issues for a given site or group of sites.
- A Technology Readiness (TRL) Level of 6 is estimated for the current system. The TRL 6 assessment is based on engineering / pilot scale, prototypical system demonstration in a relevant project environment. TRL levels 7 and 8 could have been easily achieved if a CCS site had been available for deployment of the PEM technology.
- Website: www.pem-carbon.com.

## 4.0 Project Organization, Participants and Field Deployments

The project was organized as shown in Figure 1 along with project participants including, the Kansas City Plant (Kansas City, MO), Perkin Elmer (Waltham, MA), Lincoln Laboratory (Lexington, MA), Lawrence Berkeley Lab (Berkeley, CA), LICOR Inc. (Lincoln, NB), Axys Technologies (British Vancouver, CA), Boston University (Boston, MA) and Indiana University (Indianapolis, IN). Jenifer Lewicki, Lawrence Berkeley Laboratory, served as field project Principal Investigator for PEM for natural $CO_2$ analog sites.

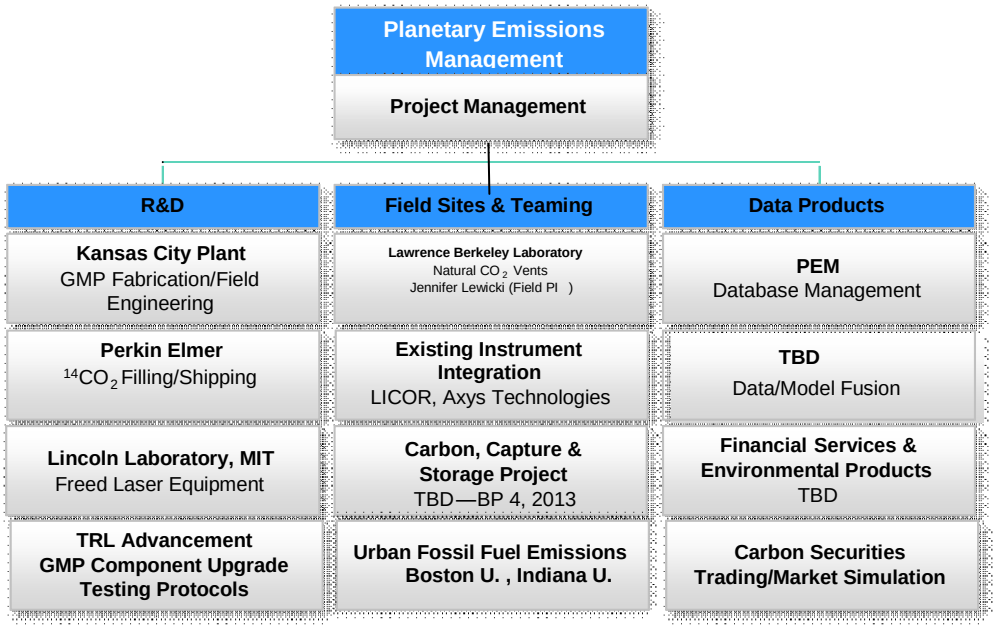


Figure 1. PEM Project Organization and Participants.

The field deployments consisted of:

1) $CO_2$ analog site, Mammoth Mountain, CA, 2010, J. Lewicki, field PI (Lewicki et al. 2011).

2) $CO_2$ analog site, Soda Springs, ID, 2011, J. Lewicki, field PI (Lewicki et al. 2012) (photos Figure 2).

3) Mega-city atmospheric sampling, Boston University rooftop, Boston, MA, 2012.

4) City scale, tower gas sampling, Indianapolis, IN, 2013.

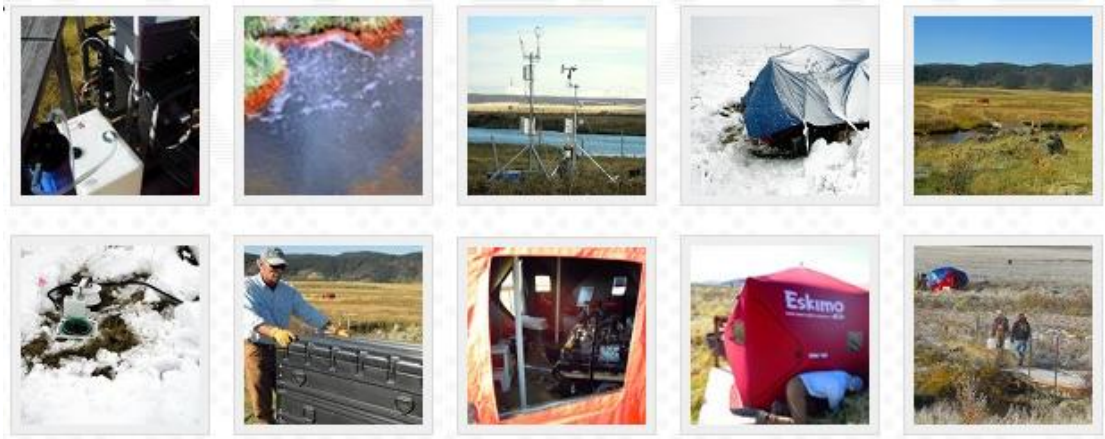


Figure 2. http://www.pem-carbon.com/field-site-activities-at-soda-springs.

**5.0 System description and Methods**

The GMP configuration is shown in Figures 3 and 4 and is described in Marino et al. (2011). Referring to Figure 1, gas was accepted from the free atmosphere, soil gas accumulation chambers and as exsolved $CO_2$. Again referring to Figure 1, the core of the system was comprised of three lasers, one each for $^{12}CO_2$, $^{13}CO_2$ and $^{14}CO_2$ species configured with piezoelectric (PZT) controllers within laser cavities defined by mirrors (M). A gas sample was drawn into the system and passed through a Nafion filter (N; Perma Pure PD Series) to remove water vapor and additional scrubbers for hydrocarbons and particulates were employed at the gas sample inlet. A mass flow controller (MFC; MKS 640, Absolute Pressure Controller, 10 Torr Full Scale, +- 0.01 Torr) maintained a constant flow rate and pressure as the sample moved first to the $^{12}CO_2/^{13}CO_2$ flow-through cell (ZnSe windows) and then through the $^{14}CO_2$ flow-through cell (Brewster angle and ZnSe windows) (Sample Cells); an oil-less scroll backing pump (Pump: Airsquared, V10T) evacuated the sample cell volumes and served as an exhaust for the analyzed gas. As the lasing action illuminates the sample gas stream causing ionization of the selected $CO_2$ isotopologue (Laser Transitions) the laser light, modulated by mechanical choppers, simultaneously passed through sealed reference cells (Sealed Cells) providing a self-contained stable reference baseline for each measurement of the sample gas stream.

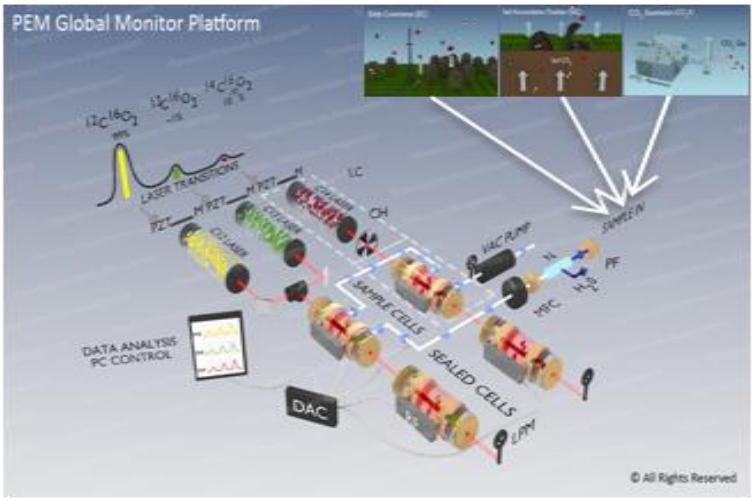


Figure 3. GMP Component Illustration and Gas Sources.

All laser pathways were longitudinal to the cells; the $^{14}CO_2$ cell, located inside the $^{14}CO_2$ laser cavity (LC), was isolated from the $^{12}CO_2$ and $^{13}CO_2$ cells to eliminate technical noise interference. The sample cells and sealed reference cells maintained active plasma discharges generated by radio frequency (RF) action on the gases present in each cell. Changes in impedance across the plasma discharge were detected by copper foil anodes and cathodes on each cell and provided a quantitative optogalvanic voltage (*OGV)* measure for each $CO_2$ isotopolouge. The signals were detected by a companion oscillator circuit coupled to the RF generator resulting in changes in gas impedance proportional to the amplitude of the RF signal; all data were passed through a Data Acquisition board (DAC; National Instruments Company) and were visualized and stored by a local PC that also ran the customized operational software (LabView 2010; National Instruments Company). Raw OGE data were acquired at 1 kHz, processed using 1 second Fourier transformations (e.g., 1 Hz sample rate) and used in computations resulting in final delta values for $^{12}CO_2$, $^{13}CO_2$ and $^{14}CO_2$ .

Ratios of *OGV* for sample and reference values eliminated laser power fluctuations and yielded the delta values directly. The emission profiles of the three single mode longitudinal lasers were characterized using a Bristol Spectrum Analyzer (model 721) with a


- Components
  - 1. All weather enclosure w wheels
  - 2. Power supply control
  - 3. Laser electronics control
  - 4. Remote operation battery pack (~6 hr operation with chiller (not shown)

Figure 4. GMP Field Components.

spectral resolution of 2 GHz and input power of ~ 5 mW. The spectral output of the $^{14}CO_2$ laser revealed a single laser peak with wavelength of 11767.522 nm with line width of 2 GHz based on full width half maximum (FWHM) representing the P(20) lasing transition identified by Bradley et al. (1986) (e.g., 849.7818 $cm^{-1}$). The line width resolution was limited to 2 GHz by the spectral analyzer. The $^{14}CO_2$ emission profile was stable over 10 measurement periods of 10" and was recorded without the use of a PZT controller to actively adjust cavity length. The P(20) lasing transition was dominant and highly stable in the "free-running" configuration and employed for the laser operation for the work described here. Data for $^{12}CO_2$ (Access Model Lazy4Z) and $^{13}CO_2$ (Access Laser Model Lazy5Z) laser outputs showed primary peaks with wavelengths of 10571.058 nm and 11127.538 nm, respectively. Minor secondary peaks of intensity for $^{12}CO_2$ and $^{13}CO_2$ were also observed with wavelengths of 10551.562 nm and 10632.017 nm, respectively, despite active PZT control. The output power for the laser system employed for $^{14}CO_2$ but filled with $^{12}CO_2$ yielded 6.1 W at 14 ma in a bench top resonator. However, the $^{14}CO_2$ output was diminished by ~50% due to Fermi resonance reducing the gain for isotopic species (e.g., Freed 1982; Silver et al. 1970). Employing a gain coefficient (e.g., $\alpha$, % $cm^{-1}$) of 0.55 for a $^{14}CO_2$ laser with a fill approximately the same as used in the system described herein reported by Freed et al. (1982; Table II), we estimate the output

power of the $^{14}CO_2$ laser at ~3 W for the P(20- Band I)) transition. We note that output laser power for a $^{14}CO_2$ laser reported by Wendland et al. (1998) employing similar input power resulted in an approximately 50% reduction in output power (3.5 W) compared to a $^{12}CO_2$ laser using a similar resonator configuration (6W) for the P(20) line. We estimate circulating laser power of approximately 60 W by considering a transmission of 5% of the output coupler. The three lasers were power modulated using optical choppers allowing OGE frequency signal differentiation representing isotopologues of $CO_2$. The portable GMP platform measured 3.5' x 3' and weighed approximately 200 pounds. Laser outputs were monitored with thermopile Vega Laser Power meters (LPM; Ophir Ltd).

The optogalvanic hardware included two pure copper sleeves epoxied to the glass cells (~ 1 cm width, 2 mm thickness, approximately 2 cm gap) with soldered wire leads. The wire leads were connected to a solid state radio frequency excitation and detection module (e.g., May & May 1986). Data were collected after ignition of a plasma in the sealed cell with a brief high voltage discharge (e.g., Marino et al., 2011). Data for the OG reference cells are expressed in volts (*OGV*) representing a voltage change across the plasma. Laser power was monitored using laser power meters (LPM; Vega, Ophir Corporation). The $^{14}CO_2$ sample cell was placed within the laser cavity (LC) of the $^{14}CO_2$ laser, and a corresponding single reference $^{14}CO_2$ cell was placed outside of the cavity. The $^{13}CO_2/^{12}CO_2$ cell served as reference for both $^{12}CO_2$ and $^{13}CO_2$ lasers as described in Figure 1 and in Marino et al. (2011). NOAA gases were prepared by the Institute of Arctic and Alpine Research (INSTAAR) University of Colorado, Boulder, CO, according to INSTAAR standard protocols and references (e.g., INSTAAR). The NOAA gas references were used to calibrate and inter-calibrate the GMP in the laboratory and the field. The GMP was optimized for $^{14}CO_2$ laser performance; data for $^{13}CO_2$ are described but represent non-optimized configurations that can be readily upgraded.

Delta Value Calculations and Data Handling. The GMP provided 1 Hz Fourier transformed *OGV* data for $CO_2$ sealed reference cells and flowing gas sample cells. The following data streams of isotopologues as recorded and calculated activity ratios (*OGV)* were captured and stored in a spreadsheet as follows:

1) $^{12}CO_{2\ sam}$; $^{12}CO_{2\ ref}$

2) $^{13}CO_{2\ sam}$; $^{13}CO_{2\ ref}$

3) $^{14}CO_{2\ sam;}$ $^{14}CO_{2\ ref}$

4) $^{12}CO_{2\ sam}$ / $^{12}CO_{2\ ref}$ = R12

5) $^{13}CO_{2\ sam}$ /$^{13}CO_{2\ ref}$ = R13

6) $^{14}CO_{2\ sam}$ /$^{14}CO_{2\ ref}$ = R14

7) R13/R12 = $\delta^{13}C$

8) R14/R12 = $\Delta^{14}C$

Expressions 7 and 8 yield the delta ("$\delta$, $\Delta$") values directly by use of the calibration regression curves (manuscript in preparation). The NOAA NIST reference materials for $\delta^{13}C$ (IRMS) and $\Delta^{14}C$ (AMS), were PDB (e.g. NIST PDB) and Oxalic Acid (e.g., NIST Oxalic acid) standard reference materials, respectively, employed by INSTAAR. GMP sample run times for standard NOAA gases were 5 to 10". The *OGV* data were analyzed using a National Instruments LabView program (NI, software program employing typical components such as PID toolkit, DAQ drivers and data acquisition cards). Resulting data represent coherent waveform averages reported in *OGV*. After data collection all values more than 5 standard deviations from the mean were eliminated as outliers. The remaining data were smoothed employing a Savitsky-Golay filter with averaging windows of from 1 to 100 seconds (AutoSignal 20012) as indicated in data results. The ratio calculations for expressions 4 to 8 greatly reduce fluctuations in the data as

each data point represents synchronous data for a sample and reference cell. Variance, such as fluctuations in laser power and technical noise, that affects both reference and sample cells were effectively removed.

Measurements. Non-resonant effects were characterized by the analysis of $CO_2$ free air as well as technical noise checks due to electronics and plasma operation on a regular basis. Electronic noise was characterized with lasers and plasma cells with and without gas and under vacuum with lasers and plasma cells in the on and off configuration. NOAA gas cylinders were analyzed at the beginning of each day in the field in random order to provide GMP calibration data. Canister gases characterized by AMS were also analyzed randomly in the field.

## 6.0 Results and Publications In Preparation

Detailed results will be available pending peer reviewed manuscripts in preparation as follows (NB: subject to revision):

- Description of the GMP electronics, operation and results for NOAA characterized gases were submitted to the *International Journal of Greenhouse Gas Technology*. The initial submission of the manuscript was declined as it lacked examples of applications data and was considered too technical for the journal. We have revised the manuscript to include an applications example and will resubmit to a more technically oriented journal.

- Results for integration of the Axys $CO_2$ extractor with the GMP.

- Results for integration of the LICOR eddy covariance system with the GMP was submitted to the *International Journal of Greenhouse Gas Control*. The response was to resubmit subsequent to the submission of the primary paper on the operation and calibration of the GMP. We have made additional improvements to the manuscript.

- Results for integration of the LICOR soil accumulation chambers with the GMP.

- Overview and summary of all results for Soda Springs and relevance to CCS leakage applications.

- Data analysis of the Boston University data may provide the basis for a publication with BU researchers.

- Data analysis of the Indianapolis, IN, site may provide the basis for a publication with U. Indiana researchers.

- Design and financial structure of a unique CCS public security linked to long term containment of CCS $CO_2$ with a case study.

- Public outreach and education through illustrations describing the 3C's of the carbon cycle. The series of illustrations titled "Carbon Codex" are in process. The initial graphic is shown in Figure 5 below.

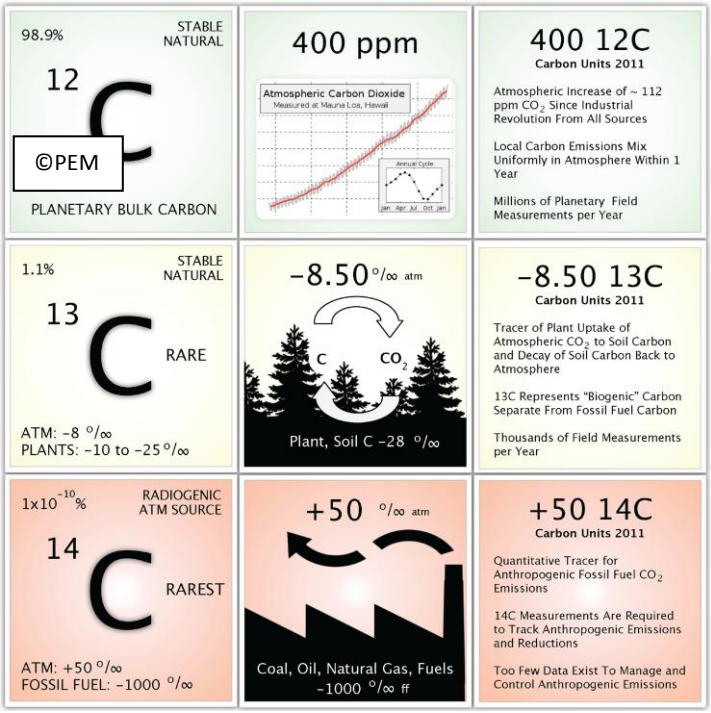


Figure 5. 3C's of the Carbon Cycle Graphic.

## 7.0 Key Recommendations Based on Results-to-Date

The key recommendations based on the results-to-date are as follows:

- Given the importance of reliable and verifiable leakage data for CCS economic success and public acceptance, $^{14}CO_2$ sampling should be mandated at CCS sites with sufficient temporal and spatial coverage to detect and quantify low levels of leakage using all available $^{14}CO_2$ measurement systems including the GMP, AMS flask sampling, passive trapping of $CO_2$ for integrated AMS measurements and new methods under development.

- Additional funding for further development of the GMP multi-isotopic analyzer platform is warranted to leverage the work completed to-date and including all non-AMS approaches for $^{14}CO_2$ such as cavity ring down, quantum cascade lasers and optogalvanic spectroscopy. Substantial improvements in GMP function and precision can be achieved with comparatively modest incremental funding.

- Deployment of the GMP analyzer with integrated eddy covariance, soil accumulation chambers and $CO_2$ exsolvation analyzers within active CCS, CCUS and EOR sites is warranted to characterize the GMP capability for such facilities at the project scale. TRL levels of 7 and 8 could be easily achieved with a brief deployment (e.g., two weeks) of the GMP in an active CCS setting.

- Compound indicators of leakage and ranges of detection limits across leakage scenarios should be explored in the field by combining short term tracers, GMP and flask sampling for isotopic analyses, diverse vadose zone and bore-hole sampling and seismic data.

- Continued modeling to explore applications of unique CCS financial instruments to cost reductions and public participation in CCS support is warranted. A CCS financial instrument demonstration project is warranted with a suitable CCS facility partner.

- Design of CCS-GMP networks across single sites, groups of sites and across regions is warranted as demonstration of a transparent CCS economic, containment performance and EHS reporting system for advanced US CCS capability benefitting all stakeholders.

- Continued efforts to engage the public with accessible information and visualizations of the underlying scientific basis for CCS performance and ways for the public to invest in CCS at the project and regional levels.

## 8.0 Summary & Conclusion

The value of continuous field-based $^{14}CO_2$ measurements in the context of monitoring, verification and accounting for CCS leakage is recognized but applications have been limited by the lack of non-AMS field methodology. The instrumental, sampling scale and potential regulatory and financial perspectives (summarized in Figure 6) developed during this effort are feasible and commercially viable. Long term CCS success requires unequivocal and transparent reporting of containment performance in the vadose zone to ensure public health and safety and verify capital investments for CCS project function. The work supported in this effort clearly demonstrates the potential of a unique field system for $^{14}CO_2$ measurements. However, as with many emerging technologies, notwithstanding the fundamental scientific basis for the approach, additional work and validation of the technology and specific applications are required. The work performed in this project has laid a foundation for incremental improvements of the GMP system with additional funding. Commercial development of the GMP and its key components including the $^{14}CO_2$ laser is achievable. The GMP can be integrated with any source of gas for analysis of the atmosphere, soil gas and dissolved $CO_2$ in the aqueous phase offering access to the key biospheric components involved in CCS leakage pathways. A unique financial CCS instrument linked to project level isotopic data for containment verification is achievable offering biospheric, economic and public benefits to all stakeholders. In conclusion, the GMP technology and financial instrument is suitable for CCS demonstration with the appropriate industrial partner filling the gap imposed on this project by lack of functioning full-scale CCS facilities.

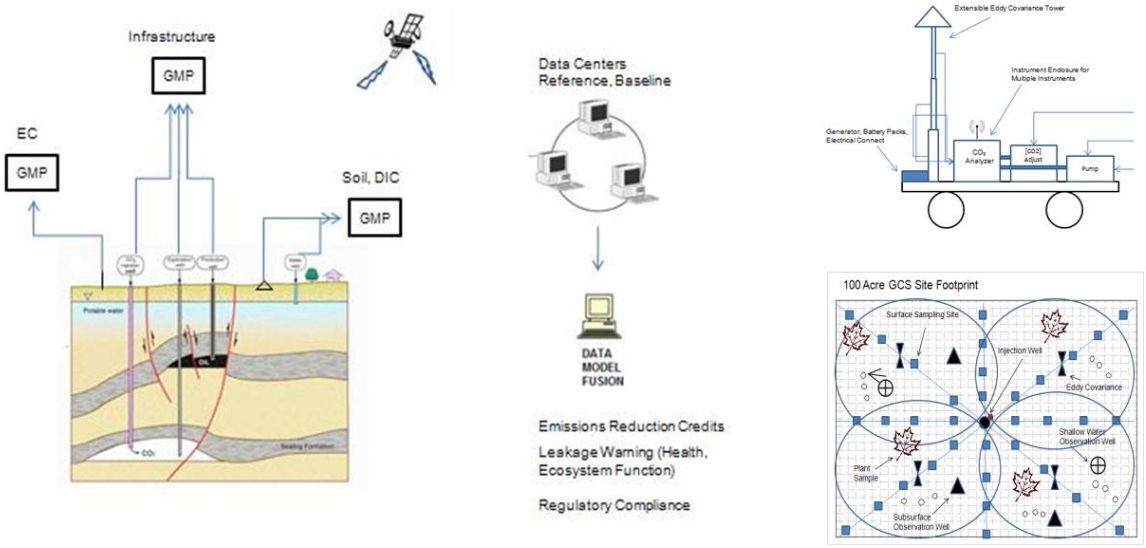


Figure 6. GMP CCS illustration showing potential commercial scale-up across a CCS site or sites, transformation of data to support carbon credits, securities and EHS and regulatory functions. Mobile deployment of instruments allows for flexible placement of integrated instrumentation (EC-eddy covariance, Infrastructure-bore hole/observation wells, gas transfer infrastructure, Soil and DIC- soil accumulation chambers and exsolvation of $CO_2$ from aqueous samples including groundwater and overlying ecological zones) within a CCS project site.

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