## ATMOSPHERIC CO<sub>2</sub> MONITORING SYSTEMS --- A CRITICAL REVIEW OF AVAILABLE TECHNIQUES AND TECHNOLOGY GAPS

REPORT FOR SMV GROUP, THE CO<sub>2</sub> CAPTURE PROJECT (CCP)

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#### **Executive Summary**

This report for the Carbon Capture Project provides information concerning the measurement of carbon dioxide in the ambient air. Monitoring for CO<sub>2</sub> should be an integral part of any sequestration project where this greenhouse gas is injected deep underground. It is appropriate to use a variety of CO<sub>2</sub> measurement methods to meet the monitoring objectives of 1) assuring there are no large leaks that might pose a safety or immediate health risk, and 2) verifying that the injected carbon dioxide indeed remains trapped below the Earth's surface. Thus the report considers detection methods ranging from personal monitors that might be worn to warn a project employee of very high local concentrations of carbon dioxide, to instruments mounted in satellites to detect over many square miles any subtle increases in CO<sub>2</sub> that might be associated with a leakage of the injected greenhouse gas back to surface.

The greatest challenge and probably most important application is the long-term, continuous measurement of CO<sub>2</sub> near ground level across the several square miles of a project area, and the immediate surrounding area. Options include 1) remote sensing from satellites or aircraft, 2) development of new open path instruments that can sample over significant distances, or 3) a large network of conventional fixed point detectors. NASA indicates satellite surveys might be useful for a "global" view of CO<sub>2</sub> although they may be limited to two-dimensions (satellites do not sample at ground level, but over the entire air column, from the surface to the stratosphere). Aircraft surveys may be an efficient means to collect data near ground level, but this is only practical in an infrequent basis. Novel instruments located on the ground that are based on open path sampling appear to offer a good compromise. They could have the capability to detect increases of just a few percent of CO<sub>2</sub> from normal background, over a sample path of 10's of meters, and, importantly, continuously and with unattended operation. Potentially, just a few such instruments could provide efficient long-term monitoring over a large area. Many different commercial fixed-point units suitable for networking are available, but this is probably an impractical approach to monitor more than a small area. These detectors are better suited for deployment to monitor sensitive, high-risk points of leakage. Infrared spectroscopy detection based methods are the most common technical approach for CO<sub>2</sub> measurement in ambient air.

This report also discusses other novel approaches to carbon dioxide monitoring. For example, one technology development in progress is the real-time measurement of carbon and oxygen isotopes via laser spectroscopy. This technique could aid in pinpointing the source of the measured CO<sub>2</sub>. Another example is the efforts by NASA to use satellite data to determine the changes in the biomass (e.g. changes in forest cover) over large areas. These observations provide a method to monitor carbon sinks over a wide area, and also are related at least indirectly to changes in greenhouse gas concentrations. CCP is sponsoring at LLNL a similar approach where remote sensing is used to monitor changes in local fauna as indicators of elevated CO<sub>2</sub> concentrations.

#### **Recommended Further Studies and Activities**

- 1. Development should be encouraged for a long, open-path laser spectrometer instrument to measure CO<sub>2</sub> in the ambient air. Potentially, a single such laser device positioned near ground level could cover a radius of several square miles. Such a device would have the distinct advantages of 1) continuous monitoring, 2) accuracy to within a couple of percent, and 3) remote and unattended operation.
- 2. Further discussions are encouraged with NASA with regards to their research activities and plans for monitoring greenhouse gases. NASA has several separate research efforts that bear directly or indirectly on the CO<sub>2</sub> monitoring requirements for CCP.
- 3. Track future developments in laser/detection technology because improvements in this hardware can aid in creating more cost-effective CO<sub>2</sub> measurement devices.
- 4. Use ongoing CO<sub>2</sub> sequestration project sites such as at Weyburn Field as test beds to evaluate and develop further CO<sub>2</sub> monitoring concepts.
- 5. Track further developments in laser spectroscopy technology that can measure in real time carbon and oxygen isotopes; such data could serve as tracers for the fate of transported or injected CO<sub>2</sub>. This approach would complement the ongoing CCP supported project that is evaluating isotopic analysis of noble gases as a tracer for gas migration in sequestration projects.

#### $\underline{Summary\ Comparison\ of\ CO_2\ Monitoring\ Methods\ --\ Niches/Advantages/Disadvantages}$

Measurement Type	Description, Application	Sensitivity/Cost for Ambient Air	Advantages	Disadvantages
	Application	Sampling		
Satellite	Remote sensing,	Costs can be of the	Covers very large	Only a "2 –D view",
	Potential to cover	order of \$10 <sup>4</sup> to \$10 <sup>5</sup>	area.	not sample at ground
	100's of square	per survey.	Technology	level for direct CO <sub>2</sub>
	miles/survey.	NASA claims can	development	measurement.
	For infrequent	resolve to 100 ft <sup>2</sup> .	sponsored at least in	Available satellites
	large area sampling	Hyperspectral	part by the	might not cover
		survey can resolve	government.	project area.
		to a few meters		
Airborne	Remote sensing,	Estimated at	Cover large area	Only practical for
	Potential to cover	\$1,000's per survey.		occasional
	10's to 100's of		Fairly fast over 10's	"snapshot"surveys.
	square miles.	Single measurement	of square miles	
	For infrequent	to 3%+/-		
	sampling.			
Open Path Laser	Ground level,	Estimated \$1,000's	Potential for one	Technology for long,
Spectrometer	Potential to cover	per unit.	fixed instrument to	open light path
	several square		cover large area.	detection is still under
	miles with 1	Instrument needs	Measurement could	development.
	device. Can be	development, but	be automated,	
	main instrument	estimate can be	continuous,	
	for long-term	3%+/- or better		
	monitoring.			
Fixed point detectors	Ground level,	Fairly cheap, (circa	Fairly cheap and	Only measures CO <sub>2</sub> at
		\$1,000)	proven technology.	the detector location
	Sample at single	Routinely better	Best used a points of	Require multiple
	fixed points of	than 3%+/ Less	higher risk	sensors to sample even
<u> </u>	high risk of leaks.	than 1%+/- available		a small area
Portable detectors	Personal protection	Very cheap; units	Very cheap;	Only suitable for spot
	and scan for	can cost <\$500	Can move to suspect	checking CO <sub>2</sub>
	equipment leaks	Better than 5%+/-	"hot spots"	concentrations

#### **Background/Objectives of this Study**

We were commissioned by the oil industry, via the CCP (Carbon Capture Project), to perform a review of  $CO_2$  measurement methods that might be employed in conjunction with subsurface  $CO_2$  disposal projects. One general requirement for carbon dioxide underground storage/disposal projects is to monitor the atmospheric  $CO_2$  at or near the earth's surface. The overall objective is to locate rapidly any minor and major leaks of carbon dioxide. Desirable attributes for such monitoring tools include: 1) low cost, 2) accurate and sensitive measurements of  $CO_2$ , 3) method can focus on a small as well a large surface area, 4) remote, automated operation, 5) reliable and safe to use. This review characterizes different carbon dioxide measurement techniques for  $CO_2$  concentration in the ambient air by sensitivity and potential area of coverage.

An important requirement for CO<sub>2</sub> subsurface disposal projects is to monitor the near-surface atmosphere for indications of leakage of CO<sub>2</sub>. Such a monitoring program will have to be conducted continuously in order to assure the public and the project employees that there are no significant gas release and hence a risk to human health. Another motivation to monitor CO<sub>2</sub> continuously is to ensure that the project is a technical success; that injected CO<sub>2</sub> indeed is sequestered successfully, permanently below ground. This requires a long-term monitoring program. Identifying quickly any minor/major failures of surface equipment or a leakage from the subsurface back to the atmosphere is desirable in order to be able to perform repairs in a timely manner.

 $CO_2$  is a relatively benign chemical, but if there is a large gas release, that event could pose a risk to human health. Carbon dioxide concentrations exceeding 1000 ppm (0.1%) cause noticeable symptoms in some people (drowsiness, headaches, "sick building syndrome"). The OSHA (Occupational Safety and Health Administration) maximum acceptable level is 5000 ppm. 2% will cause a 50% increase in breathing rate, and at 8-15%, nausea, vomiting and loss of consciousness.

Because the natural background concentrations of  $CO_2$  are 300 - 400 ppmv in ambient air, one needs only to determine if there is a <u>very</u> significant change (more than double over typical levels) in concentration before there are any human health concerns. On the other hand, if one wishes to monitor more subtle increases in  $CO_2$  atmospheric concentration with the objective of early, low-level leak detection, then the requirements become more stringent. We speculate that operators of carbon sequestration projects might require monitoring methods with sufficient sensitivity to detect increases in  $CO_2$  of 10 - 30 ppmv, or a few percent above its concentration in ambient air.

Monitoring is required on several geographic scales:

- Large scale even beyond boundaries of project cover 10's of square miles
- Within project boundaries and at the "fence line" cover several or more square miles
- At higher risk points of leakage at the field site such as wellheads and compressors, etc.
- Inside or near control rooms where workers are located
- Personal monitors for workers who travel to any higher risk areas.

We anticipate different monitoring "tools" will be required to fulfill all the potential measurement requirements for a CO<sub>2</sub> sequestration project. For monitoring very large areas, we would anticipate instrumentation mounted in satellite or more likely, low-flying aircraft could be a practical approach. Within a project area, occasional remote sensing, or novel sensors that can measure CO<sub>2</sub> over open path lengths of 100's of feet may be attractive. Fixed CO<sub>2</sub> sensors could play a role at critical points in the facilities such as near compressors in control rooms. Finally, there are a number of portable CO<sub>2</sub> detectors that should be suitable for individual employees to use when entering higher risk areas.

#### Review of Schemes for Detecting CO<sub>2</sub> Concentrations in Ambient Air

Although there are number of different approaches for  $CO_2$  detection, variations of infrared (IR) are the most common scheme for  $CO_2$  monitoring in the ambient air. Below we summarize this and other technologies and their applications.

#### Infrared analysis -- general background

CO<sub>2</sub> has unique absorption bands in the IR for analysis at different sensitivity. Below is a table of the absorption strength at different bands below 5 micron for CO<sub>2</sub>.

#### Table 1.

Wavelength(µm)	Relative Absorption strength
1.432	1
1.570	3.7
2.004	243
2.779	6800
4.255	69000

Infrared analysis in the open air can directly measure the bulk  $CO_2$  concentration. The band chosen for  $CO_2$  analysis is based on its absorption strength and the potential interferences from other gases. High absorption bands (such as at 4.25 micron) can detect very low concentrations of  $CO_2$  over even a short sample path length. Such bands, however, are then limited in their maximum concentration detection limit or path length before over saturating the detector. Bands with low absorption of  $CO_2$  are more suitable for measuring high concentrations of  $CO_2$  or to measure its concentration over a long path length. All measurements for  $CO_2$ , of course, are preferred in bands that do not overlap with wavelengths where other, potentially interfering gases, exhibit significant absorption.

The principle is to measure the absorption of IR light passing through a confined gas cell. The light is usually generated with a metal filament, giving out radiation from 3-10 microns and a power of several microwatts. The IR radiation is then filtered and only the portion corresponding to  $CO_2$ 's absorption (e.g. 4.25 micron) is used to probe the absorption of the gas in the sample cell. The detector is a MCT (Mercury Cadmium Tellerium, HgCdTe) detector with TEC (Thermal Electric Cooling).

Due to the very strong absorption by  $CO_2$  and relatively low absorption by other gases, IR spectroscopy around 4.25 micron is very sensitive for detecting  $CO_2$  in the open air. Most fixed and portable commercial  $CO_2$  monitoring systems are based on IR absorption and use a very short optical path (at most several inches long) at this band along with a filament light source.

The second strongest absorption band by  $CO_2$  is around 2.7 micron; the relative absorption strength here is about  $1/10^{th}$  of the absorption strength at 4.25 micron. This band is also very sensitive and relatively free of interference from other gases. It has been used, for example, to measure  $CO_2$  levels by the Mars Explorer by NASA. This band was chosen because the absorption strength is still strong enough for sensitive detection in a limited optical path (~100 m). However, there are no commercial diode lasers for this band and NASA had to develop a tunable laser source by itself. The strong absorption also does not allow this band to be used for  $CO_2$  detection over a long beam path either.

One other band is the 4.41~4.45 micron band, which is the absorption band for <sup>13</sup>CO<sub>2</sub>. Because <sup>13</sup>C occurs at a much lower level than <sup>12</sup>C (about 1/100<sup>th</sup> as much), this band allows detection of much higher level of total CO<sub>2</sub>. By detecting the <sup>13</sup>CO<sub>2</sub> level one may estimate the total CO<sub>2</sub> level from the isotopic ratio of <sup>13</sup>C and <sup>12</sup>C. This method allows detection of much higher concentrations of CO<sub>2</sub>, up to 0.27% with a path length of 200 m. However, because the isotope ratio of <sup>13</sup>C and <sup>12</sup>C varies from site to site, this approach is not generally reliable unless one has an independent measurement of that ratio. (See Appendix A for some further discussion about isotopic measurements.)

Another potential band is the 2 micron band (the  $v_1 + 2 v_2 + v_3$  band), with the absorption strength for  $CO_2$  at 2 microns being at least 250 times weaker than at 4.25 micron. The interferences of other gases are also much weaker than  $CO_2$  if a narrow light source is used as the probe. This weak absorption band has already been used for detection of  $CO_2$  in combustion environment  $^1$ .

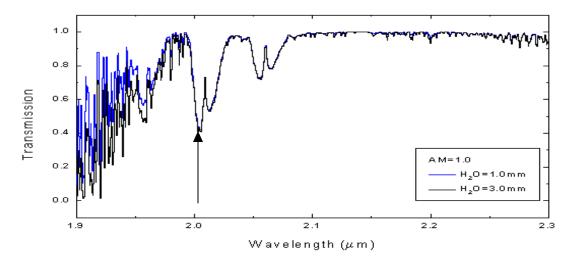


Figure 1. Air transmission at 2.01 micron; demonstrates the relatively less absorption by  $CO_2$  at this band.

There are two major advantages of detection  $CO_2$  at 2.01 micron. One advantage is the availability of lower cost DFB (Distributed Fiber Brag) diode lasers with very narrow (0.01cm-1) bandwidth at this band compared to the QCL (Quantum Cascade) lasers at 4.25 microns. The other advantage is the availability of InGaAs detectors with much better signal to noise ratio compared to MCT (HgCdTe) detectors for 4.25 micron. Based on the absorption strength of  $CO_2$  at this band, we expect one can measure  $CO_2$  concentration as high as 0.5% over a path length distance of 200 m.

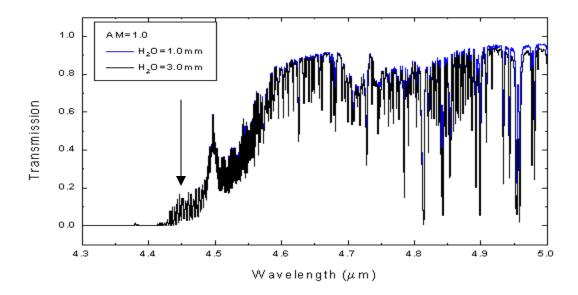


Figure 2. Air transmission at 4.45 micron is much weaker (about 50%) than at 2.01 micron. (Figure 1 and Figure 2 are simulation data by Lord, S.D. 1992, NASA Technical Memor. 103957, can be accessed at <a href="http://www.gemini.anu.edu.au/sciops/ObsProcess/obsConstraints/ocTransSpectra.html#Near-IR">http://www.gemini.anu.edu.au/sciops/ObsProcess/obsConstraints/ocTransSpectra.html#Near-IR</a>)

There is a third band at 1.57 micron for the adsorption of  $CO_2$ 's overtone ( $2v_1 + 2v_2^0 + v_3$ ). The absorption by  $CO_2$  at this band is much weaker (close to 1/100) than the band at 2.01 micron, and is only 1/20,000<sup>th</sup> compared to the absorption at 4.25 micron. This band is almost completely free of interference by other gases, as shown in Figure 3. This band is also where the fiber communication band (L-band) is, where we could find many commercial tunable narrow bandwidth lasers, amplifiers and filters, and detectors. This band has been investigated as a means for  $CO_2$  detection in a combustion chamber<sup>2</sup>. They found the band to be free of interference from other gases, but it is too weak for short path detection of  $CO_2$ . This very weak band is not suited for  $CO_2$  detection in a short path, e.g. a combustion chamber, but is ideally suited for long path  $CO_2$  detection at concentrations typical of ambient air.

The commercial availability of high power tunable narrow bandwidth lasers and filters in this band would allow one to use 2 lasers, one locked at a CO<sub>2</sub> absorption peak, while the other one is free of CO<sub>2</sub> absorption. These two light sources could be coupled into a single fiber and launched into the open space, and be collected together for fiber-coupled detection. This could allow accurate detection of the CO<sub>2</sub> level, regardless of signal variation caused by air turbulence and smog scattering. Based on the absorption strength of CO<sub>2</sub> at this band, we would expect to be able to detect 1% of CO<sub>2</sub> over a kilometer light path, or equivalently, 5% CO<sub>2</sub> over 200 meters.

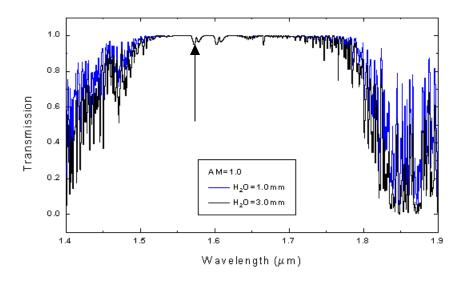


Figure 3. Air transmission at 1.57 micron is free of other gases interference, opening a potentially very useful window for a CO<sub>2</sub> probe.

The band at 1.43 micron is even weaker. Because water absorption is significant at this wavelength, this is not appropriate for detection of  $CO_2$  over a long path.

#### Infrared analysis -- long open path measurement as a newer technology

One attractive concept is to measure absorption loss (and hence CO<sub>2</sub> concentration) across a long, open-air, optical path. This has the distinct advantage of having an individual instrument collecting carbon dioxide concentration data over an extended area instead of at a single point. Such technology is in the developmental stage.

Some details of this approach are given below. Consider the set up below.

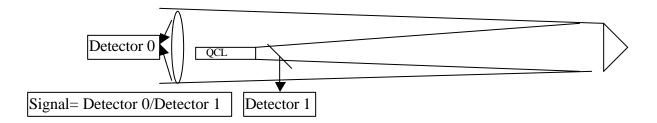


Figure 4. Concept of open path detection of CO<sub>2</sub>. A QC (Quantum Cascade) laser sends a signal out to a retro-reflector and returns to a detector. The total light path potentially can be many meters long.

Thus a single device mounted near ground level can sample many meters away. If such a device could rotate and reflect off of multiple retro-reflectors, then a single laser could sample out several direction and distances.

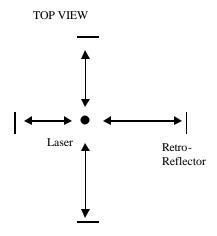


Figure 5. Possible layout for a ground level mounted open path instrument. It could send a laser pulse to several retro-reflector "mirrors" so one unit could sample over a number of distances and directions.

The disadvantage to this scheme is that the absorption (measured concentration) represents a cumulative effect over the entire light path. Thus, one cannot distinguish whether an elevated reading for carbon dioxide might represent a modest, uniform increase over the entire sample path, or could as well be from a larger jump in  $CO_2$  concentrations over a small portion of the light path. So if one were to measure a significant increase in  $CO_2$  concentrations by this method, one would have to sample further in the suspicious area more closely with perhaps a portable unit to pinpoint the source(s) of the elevated  $CO_2$  in that sampling path.

A QC laser operating with pulsed power supply can lower the average power while at the same time increase the peak intensity of the laser pulse. The expected peak power could be near 100 mW. Light out of a QC laser is collimated to have a divergence of about 1 mrad, and with a beam size of approximately 2 mm. After passing through an open air of some meters distance, the beam size will become slightly larger, where a "mirror" (retro-

reflector) will reflect the light beam back in the exact the reverse direction. When the retro-reflected beam reaches the QC laser, the size will become about twice that diameter. The crossing section of a QC laser could be very small, therefore only blocking a small proportion of the retro-reflected beam.

After the reaching the QC laser, the retro-reflected beam will be focused onto a detector and recorded. The signal is the ratio between the detector after the collection lens and the reference signal. The retro-reflector will make the alignment of the setup very easy. As long as the QCL laser is pointing to the retro-reflector, the retro-reflected beam will return in the same beam path and get collected by the lens/detector behind the QC laser.

One instrument's specification (from Air Instrument and Measurements) using a 15 cm cell and such a light source, is able to measure ambient (around 360 ppm) CO<sub>2</sub> levels with a precision of ca. 100 ppb. Beyond the 360 ppm level, the signal registered on the MCT detector falls to the same level as noise. Based on this result, with a MCT detector and a LED source which could have a spectral density ~100 times (100 microwatts spread 4-5 microns) stronger than the filament sources, one should be able to probe CO<sub>2</sub> concentration up to 360 ppm over a distance of 15 m (15cm\*100), or a *range by concentration product* of 5,400 m\*ppm. With a QCL laser operating under pulsed mode, which could give out over 10mW of power over 0.1microns, one should be able to extend the range by concentration product to 540,000 m\*ppm. For example, with a measurement optical path of 540 m, the measurable CO<sub>2</sub> concentration could be as high as 1000 ppm before over saturating the detector.

Per the previous section, one could select other wavelengths for performing the measurement where the CO<sub>2</sub> absorption is weaker (Table 1). With that approach, the light path for the sampling can be much longer, and still provide good measurement of carbon dioxide in the range of interest of circa 360 ppm. For example, the second strongest absorption band by CO<sub>2</sub> is around 2.7 micron and the relative absorption strength here is about 1/10<sup>th</sup> of the absorption strength at 4.25 micron. For the third band at 1.57 micron the absorption by CO<sub>2</sub> at this band is much weaker (close to 1/100) than the band at 2.01 micron, and is only 1/20,000<sup>th</sup> compared to the absorption at 4.25 micron. For the absorption strength of CO<sub>2</sub> at the 1.57 micron band, we would expect to be able to detect up to 1% of CO<sub>2</sub> over a light path as long as one kilometer, or a maximum of 5% CO<sub>2</sub> over a 200 meter sampling distance.

#### Solid state chemical sensors

• Based on the ionic reaction of A<sup>+</sup> + OH<sup>-</sup> +CO<sub>2</sub> = AHCO<sub>3</sub> (A: Na or Li) in phosphate electrolyte, such sensors detect CO<sub>2</sub> level by measuring the potential between the chemical sensors' electrodes. Because of the specific chemical reaction, this type of sensor is very selective. Such detectors could have linear voltage response to the log of CO<sub>2</sub> concentration when the value changes from 100ppm to 5 vol%. But, it is subject to water condensation and therefore not reliable <sup>3-7</sup>. For example, the reading of potential changed by as much as 25% when the water concentration goes up from 0.7 vol% to 30 vol% <sup>7</sup>.

- Based on a semiconductor oxides' (e.g. BaTiO<sub>3</sub> and SnO<sub>2</sub>) response to CO<sub>2</sub>. It is shown that the sensors can exhibit very good linear response to the log of CO<sub>2</sub> concentration when the sensor is made of nanocrystaline materials <sup>8</sup>. But the long term stability and signal drift of such sensors are still a problem for such detectors to become commercially available. For example, the nanocrystaline material changed its structure after several days, causing degraded sensitivity <sup>8</sup>.
- Micromechanical detectors that detect the change of mass of a polymer, which in turn responds to CO<sub>2</sub>. Such sensors are still in the developmental stage, as they also have water condensation and selectivity problems <sup>9</sup>.

All the above chemical solid state sensors could be made into very small packages, and are inexpensive in nature. But, they could only measure CO<sub>2</sub> concentration over a limited space. Many such detectors and communication network between the data center and these sensors are required to monitor the CO<sub>2</sub> concentration over a substantial area. The requirement for a large number of sensors likely makes this no longer an inexpensive proposition.

#### Gas chromatography

Of course carbon dioxide may be measured easily to within a few ppm by standard gas chromatography methods. This is not used very much now for atmospheric analysis, but it is a standard method for indoors air quality. OSHA (Occupational Safety and Health) uses this as a benchmark to compare against other proposed measurement techniques. Their application of course is to determine worker exposure to CO<sub>2</sub>. See -- http://www.osha-slc.gov/dts/sltc/methods/inorganic/id172/id172.html

#### Chemical reaction/visual indication

Another common method to measure carbon dioxide in the ambient air is the so-called "Draeger tubes". The method of detection here is based on drawing in a fixed volume of air with a hand pump through a glass tube containing a granular packed material. The material inside reacts with the  $CO_2$  brought in to create a color change. The concentration of  $CO_2$  may be read from the length of that stain. These tubes come in a variety of concentration ranges in order to improve the accuracy of the measurement.

#### CO<sub>2</sub> Monitoring Programs in Current Subsurface (EOR) Gas Injection Projects

We contacted the operators of several ongoing carbon dioxide injection projects to inquire as to the common current practices with regards to monitoring for atmospheric carbon dioxide near ground level.

For ongoing industry projects where carbon dioxide is injected for enhanced oil recovery (EOR), monitoring for CO<sub>2</sub> seems to be a fairly low priority. In particular, for projects where hydrogen sulfide is produced along with the carbon dioxide, the emphasis is placed on monitoring and preventing human exposure to any leakages of the hydrogen sulfide. For example, at Chevron's Rangely Field in Colorado and Kinder Morgan's SACROC

EOR project in Snyder, Texas, the operators are aggressive in guaranteeing that the workers or the public are not exposed to even low concentrations of very dangerous hydrogen sulfide gas. ChevronTexaco and Kinder Morgan engineers we contacted said that rather elaborate hydrogen sulfide detection schemes have been placed at selected critical points such as some wellheads, each unit costing of the order of \$3,000/installation. These installation schemes are considered state-of-the-art and include a sensitive gas detector, remote data acquisition, and an alarm system.

These operators said there were minimal legal requirements for monitoring of carbon dioxide gas as it is considered a non-toxic substance, especially as compared to typical produced hydrocarbons. Kinder-Morgan is a major producer of carbon dioxide; one engineer we interviewed said carbon dioxide detectors typically are placed only at the highest risk points such as near compressors and perhaps in control rooms. Minimal steps are taken to monitor leaks by *chemical detection methods* from carbon dioxide pipelines transporting the gas to various oil industry EOR locations. Pipeline operators rely more on changes in flow and pressure readings for indications any leakages.

New CO<sub>2</sub> subsurface injection projects where the main motivation is for sequestration of this greenhouse gas have paid more attention to monitoring issues. For example, for the GEO-SEQ project (sponsored by the National Energy Technology Laboratory) there is a focus on detection methods related to the *subsurface* migration of injected carbon dioxide. Methods being assessed include integrated high resolution geophysical techniques performed at the surface, and also crosswell electromagnetic techniques.

#### Summary of Remote Sensing Technology (i.e. NASA) for CO<sub>2</sub> Measurement

Appendix B provides a listing of some of the key scientists at three NASA sites (JPL – Jet Propulsion Laboratory/Pasadena, CA, Langely/Hampton, VA, and Goddard Space Flight Center/Greenbelt, MD) who are a potential information and technology resource for the oil industry about carbon dioxide monitoring. Appendix B includes brief highlights of several of these programs, plus there are a larger number of one-page summaries.

NASA has an active research program to study the Earth's weather and atmosphere, and global warming and carbon cycle issues in particular. These and other related NASA research areas are of potential interest to the goals of the CCP to monitor CO<sub>2</sub> concentrations at carbon sequestration projects. These other projects include advanced laser and instrumentation methods, and also the study of carbon dioxide and the other components in the atmospheres of other planets. Indirect measurement techniques offer an interesting alternative approach, such as monitoring remotely for subtle changes in the flora at ground level. In fact, CCP is sponsoring a study that is researching exactly that idea. In materials presented at the CCP sponsored conference in Potsdam, Germany in 2001, the authors claim they potentially can resolve differences in flora to a few feet. That study anticipates conducting a field test of remote sensing of flora changes at a remote CO<sub>2</sub> EOR injection project at Rangely Field, in Colorado in 2002. Yet another indirect approach presented at the Potsdam conference is the notion of remote surveys for detecting subtle changes in the surface deformation. The thought is that these changes reflect movement of pressure changes subsurface associated with CO<sub>2</sub> injection. In the conference is the conference of the changes reflect movement of pressure changes subsurface associated with CO<sub>2</sub> injection.

The common opinion we obtained from NASA experts is that satellite monitoring (or that using very high altitude aircraft like a modified U-2) using spectrometers can scan for carbon dioxide over large areas. One can resolve carbon dioxide concentrations in blocks perhaps as small as 100 square meters. If one averages over a larger area (such as a square mile) then the total measured concentration of carbon dioxide has improved accuracy. The disadvantage of these measurements is that they sample the entire air column. That is, typically these surveys provide carbon dioxide concentrations only in "two-dimensions". That is, they are not yet able to sample selectively in the 3<sup>rd</sup>, vertical dimension, and focus their detection to just near ground level, which is of primary interest to the CCP application.

Increases in  $CO_2$  levels near the Earth's surface caused by leakage of injected gas back to surface might be detected, but increases in  $CO_2$  in the upper atmosphere for other reasons also would be detected. That is, this approach might be subject to "false positives". Thus satellite data might be a convenient tool as a "screening" method to spot unusual changes in  $CO_2$  levels; but those changes may not necessarily be at ground level nor related to activity at the sequestration project.

If there are any satellites that have the correct sensors and fly over the project area, then there may be the opportunity to have data on a quite frequent basis. One might be able to take advantage of already planned and funded NASA projects to collect data of interest.

Low-level airplane surveys seem like a superior movable platform for more detailed remote measurement over a project area for the carbon dioxide concentrations near the earth's surface. One can pick and choose the exact area and the frequency of sampling. However, the cost and inconvenience of such airplane surveys make this a practical approach only for a relatively infrequent basis.

Not surprisingly, NASA has a high interest on interplanetary space exploration and high atmospheric research for Earth. <sup>14-16</sup> While perhaps not directly applicable for the oil industry, CCP concern, improved laser detection and associated measurement research could be prove useful to the CCP monitoring goals.

For example, projected research at JPL includes development of an InGaAsSb/GaSb laser that can detect spectra 2 to 5 microns, with the expectation of having a device that can operate in the next 2 years. Intersubband Quantum Cascade lasers are being developed for Mars exploration. The wavelengths are in the range of 4 to 11 microns, typically with a power of 10-20 mW.

#### **Vendor Products/Commercial Carbon Dioxide Detectors**

Appendix C has summary tables about a number of commercial carbon dioxide detectors available on the market today. In addition, the Appendix C has detailed information we received about each of these devices from the vendors directly or from their respective web sites. We consider applications for: 1) fixed (point) detection, 2) portable and personal monitors.

#### Fixed (Point) Detectors

We spent more effort on locating manufacturers of the fixed than portable detectors because this probably has more potential interest to CCP. Table C-2 has a summary of various fixed carbon dioxide detectors from 9 different vendors. There are yet other manufacturers and distributors, but our list of 9 is representative of what is available on the market.

Typically the detector itself is a NDIR (non-dispersive IR) type. The cost of just the detector can be less than \$1,000. Adding a visual readout or rudimentary data acquisition capability can increase the price to as much as \$2,000. A full gas sensor system rated as explosion proof can approach \$4,000/installation. Most of these devices are intended as room gas monitors, but some are suitable for installation outside.

Advantages of the se instruments are that they can be relatively low cost and provide indications of at least large shifts in the carbon dioxide concentration in the atmosphere. Their responses to changes in the carbon dioxide concentration are no more than a few seconds, and they have the capability to provide a continuous read out of results. A major limitation of these devices is that they typically will sample the atmospheric gases at one fixed point. Thus a great many commercial sensors would be required in order to cover a substantial geographic area. Some of these products have a sampling tube that allows for remote analysis of the air for distances from 30 to about 100 feet from the sensor.

The claimed accuracy of these instruments varies significantly. Some of the low cost devices (around \$500) are accurate to only +/-5% of full scale. Other vendors claim their instruments can achieve an accuracy of +/-2%, or better. Verris Industries, for example, suggest their CX Series of  $CO_2$  detectors are good to 1%; thus, for their detector with a range of 0-2000 ppm of  $CO_2$ , the claimed accuracy is +/- 20ppm. Li-Cor has an instrument claimed to be accurate to 1 ppm or better.

#### Portable and Personal Monitors

There is at least some concern with the exposure of project personnel to high levels of carbon dioxide gas. Because of its greater density, CO<sub>2</sub> that may arise from a leakage would tend to concentrate in low spots. Workers who are in the project area on a regular basis should have access to devices to guarantee they are getting into a dangerous area.

Carbon dioxide concentrations exceeding 1000 ppm (0.1%) cause noticeable symptoms in some people (drowsiness, headaches, "sick building syndrome"). The OSHA (Occupational Safety and Health Administration) maximum acceptable level is 5000 ppm for an 8-hour day for a worker. Carbon dioxide levels as high as 2% will cause a 50% increase in breathing rate, and at 8-15%, nausea, vomiting and loss of consciousness.

As detailed in Appendix C there are a number of small hand-held meters one may carry to check for carbon dioxide concentrations. The resolution of these devices is typically no better than 100 ppm. This is sufficient accuracy if indeed the main purpose is just to check that there are not very high levels of carbon dioxide above normal ambient

conditions (percents of  $CO_2$  versus the 300 - 400 ppm) that thereby create an immediate health risk. These portable meters commonly are less than \$1,000 each and most all of them use IR detection.

Another approach is to use so-called "Draeger Tubes". This system uses small hand-held pumps to sample the air. The air drawn in is sent through a glass tube containing a packing of granular material. The component of interest in the air (carbon dioxide in this case) reacts with the packing to create a color change. The length of the color change is proportional to the constituent concentration. Besides  $CO_2$  there are tubes available for a wide variety of vapors. The cost of each disposable tube is a few dollars.

#### **References**

- 1. (a) Webber ME, Kim S, Sanders ST, Baer DS, Hanson RK, Ikeda Y, **APPLIED OPTICS** 40: (6) 821-828, 2001
  - (b) Mihalcea RM, Baer DS, Hanson RK, **APPLIED OPTICS 37**: (36) 8341, 1998
- 2. (a) David M. Sonnenfroh and Mark G. Allen, **APPLIED OPTICS** 36: (15) 3298-3300, 1997.
  - (b) Mihalcea RM, Baer DS, Hanson RK, APPLIED OPTICS 36: (36) 8745, 1997
- 3. Aono H., **CHEM LETT**, 331,1990
- 4. Aono H., **J ELECTROCHEM SOC**, Vol 37, P. 1023,1990
- 5. Cote R., **J ELECTROCHEM SOC**, Vol 131, 63,1984
- 6. Imanaka N., **SENSOR ACTUAT B-CHEM**, Vol 13, 476,1993
- 7. Imanaka N., **SENSOR ACTUAT B-CHEM**, Vol 24, 380-382, 1995
- 8. Keller P, Ferkel H, Zweiacker K, Naser J, Meyer JU, Riehemann W **SENSORS AND ACTUATORS B** 57: (1-3) 39-46 SEP 7 1999
- 9. Cai QY, Cammers-Goodwin A, Grimes CA **JOURNAL OF ENVIRONMENTAL MONITORING** 2: (6) 556-560 DEC 2000
- 10. Anderson, Bruce, Personal Communication, NASA, Langely, Carbon Cycle Research.
- 11. Pickles, W.L.: "Geobotanical Hyperspectral Remote Sensing of Vegetation Responses to CO2 Leakage from Underground Storage Formations", presented at the CCP Carbon Sequestration Conference, Potsdam, Germany, 30 Oct. 1 Nov., 2001.
- 12. Zebker, H.A. and Harris, J.: "Monitoring the Injection and Storage of CO2 in Aquifers and Gas Reservoirs Using Satellite Radar Interferometry", presented at the CCP Carbon Sequestration Conference, Potsdam, Germany, 30 Oct. 1 Nov., 2001.

- 13. Abshire, James, Personal Communication, NASA, Goddard Space Center, Space Born Laser Development.
- 14. Carlson, Robert W.: "A Tenuous Carbon Dioxide Atmosphere on Jupiter's Moon Callisto", JPL Report, November 3, 1998.
- 15. Vane, Gregg: "Airborne Visible/Infrared Imaging Spectrometer (AVIRIS)", JPL Publication 87-38, November 15, 1987.
- 16. Vincent, Mark A. and Sasan S. Saatchi: "Comparison of Remote Sensing Techniques for Measuring Carbon Sequestration", JPL Publication, February, 1999.

## APPENDIX A. ISOTOPE ANALYSIS FOR CARBON DIOXIDE IN REAL TIME VIA LASER SPECTROSCOPY

#### Background

Discussions with Dr. Mark Zahniser of Aerodyne Research, Inc. reveal they have an active research program sponsored by the Department of Energy to develop a real time measurement of the isotopic compositions of carbon dioxide and methane. Their objective is to create a unique tool for monitoring greenhouse gases in the atmosphere. Their concept for convenient, real time measurement of isotopic compositions may have a use in CO<sub>2</sub> monitoring in sequestration projects such as envisioned by CCP.

Measurement of isotopes could be useful in detecting the source of a sample of CO<sub>2</sub>. One key requirement would be that there is a significant isotopic shift in the carbon dioxide in the injected gas versus that in the background atmosphere. That is, the isotopic composition of the injected gas might serve as a "tag" so that one could identify CO<sub>2</sub> that came from the disposal gas versus the CO<sub>2</sub> naturally present in the local atmosphere. For example, carbon dioxide in combustion gas (such as from a power plant that is slated for disposal) is likely to have a different, lower <sup>13</sup>C/<sup>12</sup>C ratio versus that normally found in the atmosphere (Hoefs, 1996). The gas isotope ratio in the carbon dioxide of the injected gas, versus that ratio in normal atmospheric gas could serve as "end points". For a gas mixture with a mid-value isotopic ratio, one could calculate the CO<sub>2</sub> fraction from each source. This approach could be used, for example, to diagnose a simple mixture created by a gas leak from surface equipment into the surrounding atmosphere.

This concept of "tagging" the injected CO<sub>2</sub> by its isotopes may not work or be so straightforward for subsurface disposal projects. There are the additional complications of pre-existing CO<sub>2</sub> in the subsurface having a different isotopic composition, or that there is a shift in carbon isotope fractions caused by mineral dissolution/precipitation reactions associated with the movement of the injected gas. Thus, the isotope ratios of any CO<sub>2</sub> molecules that leak back to the surface may be in fact no the same as that for the original injection gas. The net result is that the isotopic data may or may not be too muddled to provide useful data for such projects.

CCP is sponsoring an alternative tracer concept, namely via the measurement of the isotopic ratios of noble gases (Nimz and Hudson, 2001). The author's presentation suggests noble gases with a particular signature could be included in the injected CO<sub>2</sub> to serve as tracer compounds. What we are suggesting is that careful measurement of the carbon and/or oxygen isotopes might serve a similar purpose.

"Natural" isotopic tags and their relative abundances include:  $^{13}$ C, 1.10%;  $^{18}$ O, 0.20%,  $^{17}$ O, 0.04%. While many studies have been focused on  $^{13}$ C/ $^{12}$ C values, there is the promise of additional valuable information from the  $^{18}$ O/ $^{16}$ O data. Stable isotope abundances are typically expressed in terms of  $\delta$ -units, which are based on a comparison of the ratio of a rare to abundant isotope in a sample (e.g.  $Rx = ^{13}$ C/ $^{12}$ C), to the same

isotope ratio in a standard sample, Rstd. The  $\delta$ -unit is defined as:  $\delta x = [(Rx - Rstd)/Rstd] x1000$ . To characterize a sample with a precision of one  $\delta$ -unit (1 ‰), each of the four isotopic concentration measurements must be made to a precision of better than 0.05%.

The standard method for determining trace gas stable isotope ratios is isotope ratio mass spectrometry (IRMS) (Trumbore 1995). IRMS is an extremely precise method, with  $\delta^{13}C$  and  $\delta^{18}O$  values typically obtained with precision on the order of 0.01 - 0.05 ‰. While its precision is very good the IRMS technique has a number of experimental drawbacks. Non-CO<sub>2</sub> carbon gas samples must be quantitatively separated from atmospheric CO<sub>2</sub> and completely oxidized before analysis. If the sample contains atmospheric N<sub>2</sub>O, which has the same molecular weight as CO<sub>2</sub>, the N<sub>2</sub>O must be eliminated or the mass spectra suitably corrected. Commercial IRMS units are very expensive and require permanent installation for reliable operation. Thus, field samples are normally returned to the laboratory and analyzed long after they are taken, and real time analysis is not practical.

#### Description of Isotope Analysis by Laser Spectroscopy

Aerodyne, Inc instead is developing a laser spectroscopy method that offers the potential of performing a field-deployable instrument for isotopic measurements in real-time. Their objective is to have an instrument suitable for both carbon dioxide and methane measurement. Such a device might be located at a fixed point on the ground, or perhaps deployed in a light aircraft to make occasional sweeps over the multiple square miles of area of project interest.

Specifically, they are investigating tunable infrared laser differential adsorption spectroscopy (TILDAS) techniques. TILDAS techniques, usually employing tunable lead salt diode lasers, have been widely employed for atmospheric trace gas measurements (Kolb 1995). For isotopic measurements, the high spectral resolution of tunable infrared laser techniques is particularly attractive since they are more capable of isolating spectral features for each isotope of interest. The use of TILDAS techniques to make trace gas stable isotope measurements has also been previously addressed by several research groups. The most successful spectroscopic system for environmental isotope measurement was developed by Bergamaschi et al. 1994, who used lead salt lasers to measure  $\delta^{13}$ C with a precision of 0.5 % in preconcentrated methane. Becker et al. 1992 described a lead salt laser system for  $\delta^{13}$ C measurements of CO<sub>2</sub> with a precision of 4 ‰. Giubileo et al. 2001 report a laboratory TDL system for human breath analysis, but a precision is not reported.

Spectroscopic measurements of isotopic ratios have suffered from limited precision due to the large difference in concentration of the major and minor isotopes. This is a consequence of the nonlinearity of optical transmission versus concentration. Long path lengths or increased concentrations are used to increase the absorption depth of scarce gases. If the minor isotopic constituent has sufficient absorption depth for a precise measurement, then the major constituent can have so much absorption that there is essentially no transmission at line center, i.e. the line is "black". It is difficult to achieve a precise concentration measurement using "black" lines.

Aerodyne developed an experimental system to increase the precision of TILDAS isotopic measurements. The general approach is to better balance the absorption due to the major and minor isotopes by employing an absorption cell that allows two different path lengths. They measure the minor constituent ( $^{13}C^{16}O2$ ) with a path length 72 times longer than that for the major constituent ( $^{12}C^{16}O2$ ). This length ratio approximates the natural  $^{13}C/^{12}C$  isotopic abundance ratio and thereby allows infrared transitions of nearly equal lower state energies to be used to minimize the effect of sample temperature variations, while still maintaining comparable optical depths. Since the two measurements are simultaneous within the same cell, the temperature and pressure are identical. They choose combinations of methane and carbon dioxide lines where  $^{13}C$  and  $^{18}O$  isotopes can be detected within a single sweep of the laser source and yet have a minimal difference in lower state energy. This minimizes temperature sensitivity.

A prototype optical system using a conventional lead salt tunable diode laser (TDL) and the dual-path absorption cell were used to demonstrate the measurement precision using ambient concentrations of carbon dioxide. For example, this laser could detect isotopic ratio changes ( $\delta^{13}$ C) in the air within a greenhouse ( $-0.1 \pm 0.2$  ‰) and automobile exhaust ( $-16.1 \pm 0.2$  ‰), both relative to ambient air. These results, where the uncertainty is  $\pm 2$  standard deviations, were obtained with an integration time of less than 10 minutes and sample volume of less than 3 liters.

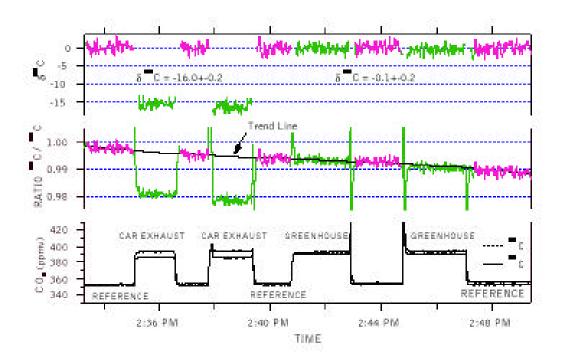


Figure A-1.  $^{13}$  CO<sub>2</sub> analysis of automobile exhaust and greenhouse air. The lower panel shows the measured concentrations of  $^{12}$ C $^{16}$ O<sub>2</sub> and  $^{13}$ C $^{16}$ O<sub>2</sub> as sample (diluted exhaust or greenhouse air) and reference (ambient air) are alternately introduced into the cell, each for approximately 90 seconds.

The middle panel shows the ratio of concentrations, with a constant drift of -0.5 % min<sup>-1</sup> The top panel shows (with the constant drift removed) the automobile exhaust  $\delta^{13}$ C of -16  $\pm$  0.2 (2 $\sigma$ ) %, and the greenhouse air  $\delta^{13}$  C of -0.1  $\pm$  0.2 (2 $\sigma$ ) %.

#### References for Appendix A,

Becker, J.F., T. B. Sauke and M. Loewenstein, APPLIED OPTICS 31 1921-1927, 1992.

Bergamaschi, P., M. Schupp and G. W. Harris, **APPLIED OPTICS** 33 7704 – 7716, 1994.

Giubiloe, G., R. Fantoni, L. De Dominicis, M. Giorgi, R. Pulvirenti and M. Snels, **LASER PHYSICS** 11 154 – 157, 2001.

Hoefs, J.: Stable Isotope Geochemistry, Springer, New York, 1997.

Kolb. C.E., J. C. Wormhoudt and M. S. Zahniser: "Recent advances in spectroscopic instrumentation for measuring stable gases in the natural environment", in P. A. Matson, and R. C. Harriss (Eds.), <u>Biogenic Trace Gases: Measuring Emissions from Soil and Water</u>, Blackwell Science Ltd., Oxford, U.K., 1995.

Nims and Hudson: "Noble Gas Isotopes for Screening, Verification, and Monitoring at CO<sub>2</sub> Storage Sites", presented at the CCP Carbon Sequestration Conference, Potsdam, Germany, 30 Oct. – 1 Nov., 2001.

Trumbore, S.E.: "Use of isotopes and tracers in the study of emission and consumption of trace gases in terrestrial environments, in P.A. Matson and R. C. Harriss (Eds.) <u>Biogenic Trace Gases: Measuring Emissions from Soil and Water</u>, Blackwell Science Ltd., Oxford, U.K., 1995.

## APPENDIX B. HIGHLIGHTS ABOUT SOME NASA REMOTE SENSING PROGRAMS

#### **Program Summaries and Contacts**

Table B -1 Research Scientist Contacts and Areas of Interest at NASA Related to  $CO_2$  Monitoring

Person	Location/Contact	Area of Interest
Webster, Christopher	JPL	Earth and Planetary
R.	(818) 354-7478	Measurements and Laser
14	cwebster@alphal.jpl.nasa.gov	Laboratory Spectroscopy
Green, Robert O.	JPL	Earth, Land, and Water
,,	(818) 354-9136	Surface Imaging
	rog@spectra.jpl.nasa.gov	Spectroscopy
Baines, Kevin Hayes	JPL	High-Resolution
,	(818) 354-0481	Measurements of Dynamical
	baines@aloha.jpl.nasa.gov	Processes in Major Planets
Pain, Bedabrata	JPL	Imaging Devices and Sensor
	(818) 354-8765	Electronics
	bedebrata.pain@jpl.nasa.gov	
McDermid, Iain Stuart	JPL	Laser Remote Sensing of the
	(619) 249-4262	Atmosphere
	mcdermid@tmf.jpl.nasa.gov	
Toon, Geoffrey C.	JPL	Remote Sensing of
	(818) 354-8259	Atmospheric Structure and
	toon@mark4sun.jpl.nasa.gov	Composition by High-
		Resolution Infrared Fouier-
		Transform Spectroscopy
Kursinski, E. Robert	JPL	Remote Sensing of the
	(818) 354-7533	Atmosphere with Global
	rob.kursinski@jpl.nasa.gov	Positioning System
Salawitch, Ross J.	JPL	The Influence of Human
	(818) 354-0442	Activity on the Composition
	rjs@caeser.jpl.nasa.gov	of the Atmosphere
Anderson, Bruce E.	Langley Research Center	Carbon Cycle Research
	(757) 864-5850	
	b.e.anderson@larc.nasa.gov	
Heaps, Wiliam Stanley	Goddard Space Flight Center	Lasers and Electro-Optics
	(301) 286-5106	Devices for Active and
	heaps@aeolus.gsfc.nasa.gov	Passive Remote-Sensing
		Instruments
Pearl, John C.	Goddard Space Flight Center	Infrared Fourier-Transform
	(301) 286-8487	Spectroscopy of Planetary
	john@chryse.gsfc.nasa.gov	Atmospheres
Stephen, Mark	Goddard Space Fight Center	Lasers and Electro-Optics
	(301) 286-3245	Devices for Active and

	mark.stephen@gsfc.nasa.gov	Passive Remote-Sensing
		Instruments
Ungar, Stephen G.	Goddard Space Flight Center	Vegetation and Soil Sciences
	(301) 614-6674	
	ungarltpmail.gsfc.nasa.gov	
Abshire, James Brice	Goddard Space Flight Center	Spaceborne Laser Sensor
	(301) 614-6717	Development
	jabshire@pop900.gsfc.nasa.gov	_

## JPL – The Influence of Human Activity on the Composition of the Atmosphere

(JPL Contact Ross Salawitch)

This group at JPL has the objective of understanding better the effects of human activity on the composition of the atmosphere. Their studies attempt to piece together the variations in the carbon dioxide and its isotopic composition during the past 200 years. They analyze observations collected from aircraft, balloon and satellite platforms to study photochemical processes that regulate the abundance of ozone in the stratosphere and troposphere.

Given that they share some of the research goals of the CCP, they may wish to participate with CCP in furthering carbon dioxide measurement technology.

### JPL - Indirect Measurement of Carbon Dioxide – via Global Warming Impacts

(JPL Contacts Mark A. Vincent and Sasan S. Saatchi -- see their paper "Comparison of Remote Sensing Techniques for Measuring Carbon Sequestration", JPL, February, 1999.)

The authors address monitoring of global warming via remote sensing from the perspective of detecting the *impacts* of carbon sequestration. Their perspective is how do we monitor for carbon dioxide control in the context of the Kyoto Protocol. This study concentrated on the NASA Earth Science Enterprise goal of finding the optimum combination of measurements and modeling to quantify the amount of carbon sequestered.

In particular, the authors focus on their attention to *changes in biomass* as a metric for the *managed* storage of carbon dioxide. For example, remote sensing potentially can verify the degree of success in efforts to implement reforestation or other planting efforts to increase a sink for carbon dioxide. Satellites can detect the progress of major forest fires or logging as threats to increasing the concentration of greenhouse gases.

(This approach is consistent with that of one project sponsored by CCP. Namely, one monitors for CO<sub>2</sub> surface leakages over a whole subsurface carbon dioxide injection project area via the study of plant life whose growth or characteristics are very sensitive to changes in the atmospheric levels of carbon dioxide. The local vegetation then could

be monitored by ground inspection or perhaps via remote methods as presented in this JPL paper and discussed further below.)

The JPL paper considers two major instrument types: 1) passive optical/infrared (IR) sensors and 2) active radar devices. The radar systems are usually designed to use a signal combination technique to synthesize a longer antenna, and hence carry the name Synthetic Aperature Radar (SAR). The major conclusion from this paper is that in order to detect changes in land transformations (e.g. changes in vegetation and amount of thawing in tundra areas) a combination of both approaches is better, with the objective of having both capable of 100 m resolution. They recommend optical/IR methods to measure changes in Land Use and Land Cover, and SAR methods to assess total biomass and its changes in a given area.

# JPL - Atmospheric Measurement of Carbon Dioxide on Other Planets (JPL Contact Robert W. Carlson, see his paper "A Tenuous Carbon Dioxide Atmosphere on Jupiter's Moon Callisto", JPL, November 3, 1998.)

The author describes a scan of Callisto, one of Jupiter's moons by the Galileo Near Infrared Mapping Spectrophotometer (NIMS) to search for carbon dioxide atmosphere. Measurements indicated the presence of a tenuous carbon dioxide atmosphere with surface pressure of  $7.5 \times 10^{-12}$  bar and a temperature of about  $150 \, ^{\circ}$ K, close to the surface temperature. The author concludes that the atmosphere is transient and was formed recently, or some process is currently supplying  $CO_2$  to the atmosphere.

The scan performed by the Galileo spacecraft during a close flyby. Spectra were obtained at bout 5 km intervals, with the instantaneous vertical resolution of less than 2 km. The search was made for characteristic airglow emissions produced by resonance scattering and fluorescence of solar radiation in the strong  $\nu_3$  fundamental stretching band of CO<sub>2</sub> at 4.26  $\mu$ m.

Other studies indicate carbon dioxide is in the stratospheres of Jupiter, Saturn, and Neptune. These projects demonstrate there is a unique capability by NASA to measure carbon dioxide under these exotic circumstances. However, these satellite surveys only the upper atmospheres of these planets.

## JPL – Earth, Land, and Water Surface Imaging Spectroscopy – AVIRIS, Airborne Visible/Infrared Spectrometer (JPL Contacts Robert Green)

Research studies include topics such as ecology, land use/land cover, natural hazards, and biological oceanography.

AVIRIS is a unique optical sensor that delivers calibrated images of the upwelling spectral radiance in 224 bands with wavelengths from 400 to 2500 nm. This instrument flies aboard a NASA ER-2 airplane (a modified U2 plane) that flies at approximately 20

km above sea level. AVIRIS uses a scanning mirror to sweep back and forth producing 614 pixels for the 224 detectors each scan. Each pixel covers about 20 square meters.

The main objective of the AVIRIS project is to measure constituents of the Earth's surface and atmosphere based on molecular absorption and particle scattering signatures. The NASA focus is on understanding processes related to global environment and climate change. One published example application demonstrating the capability for this tool involved characterizing minerals at the Earth's surface.

### JPL – Imaging Devices and Sensor Electronics and Laser Laboratory Spectroscopy

(JPL Contact, Bedabrata Pain, Christopher Webster, and Siamak Forouhar)

JPL has an active program of research in spectroscopy methods and image sensors to support the various NASA space missions. Emphasis is on sensors operating in the ultraviolet/visible/infrared (IR) spectral regions. In addition they have expertise in highenergy particle and radiation detectors, and low-noise low power electronics to support such sensors. Active research topics include low-noise cryogenic IR detector readout devices and multiplexers, system-on-a-chip development, and solid state photon and particle counting.

Improved tunable lasers techniques also are being developed for this program of atmospheric field measurements, with emphasis on the IR region. Typically, projects will have simultaneous measurement of the concentration of several species that play a role in photochemistry and transport.

Projected research includes development of a InGaAsSb/GaSb laser that can detect spectra 2 to 5 microns, with the expectation of having a device that can operate in the next 2 years. Intersubband Quantum Cascade lasers are being developed for Mars. The wavelengths are in the range of 4 to 11 microns with a typical 10-20 mW power.

## NASA Langley Research Center -- Carbon Cycle Research (Langley Contact, Bruce Anderson)

They have an ongoing effort to monitor  $CO_2$  in the atmosphere from aircraft and satellite for purposes to aid in understanding of global warming. Their objectives have included quantifying the spatial and temporal variability of  $CO_2$  in the background atmosphere as well as assessing the impact that various sources/sinks have on the tropospheric  $CO_2$  budget.

Work at the NASA Global Tropospheric Experiment Program includes laboratory tests and calibrations to improve and expand measurement capabilities especially in the area of fluxes, installation and operation of instruments on towers and aircraft, domestic and foreign deployments, reduction and archival of data, and data analysis.

For example, they are investigating methods to measure the column cycle of carbon dioxide. That is, a 2-D view of the carbon dioxide concentrations and how they change.

Instrumentation under development includes those that use gas filter correlation spectroscopy and long path length IR.

Comments from one of the researchers at Langley indicated that satellite imaging is not likely to be practical to measuring directly the near surface carbon dioxide concentrations. This is because of the limitations of detection where there is significant surface topography. His opinion was measurement from aircraft was much more practical for remote sensing for our application of most interest.

Comments from Goddard Space Center -- Lasers and Electro-Optics Devices For Active and Passive Remote-Sensing Instruments (Goddard Contact, Mark Stephen)

These devices are incorporated into Earth, planetary, and space science instruments. These devices also are used in scientific instruments including lidars (light detection and ranging), Fouier-transform spectrometers, and imaging tunable filters. Part of their effort are to develop atmospheric lidars for range resolved carbon dioxide measurement, as well as clouds, ozone, etc., and spectroscopic instruments from UV to IR.

His information is that NASA has a keen interest in the study of the global carbon cycle. Current technology can survey and map the earth in a two-dimensional view of carbon dioxide concentrations (samples the entire column of air). Resolution is possible to as low as a 100 square meters, but the accuracy improves if the sample area is as large as a square mile.

#### Comments from Goddard Space Center -- Spaceborne Laser Sensor Development

(Goddard Contact, James Abshire)

They are starting to address the technology needed to measure  $CO_2$  from space. The eventual goal is to develop a laser sensor capable of measuring  $CO_2$  from orbit continuously for a few years, furnishing the atmospheric  $CO_2$  data needed to better understand the global carbon cycle. The work is at an early stage, and they are using a differential laser absorption approach.

To date they have demonstrated CO<sub>2</sub> measurements in an gas absorption cell along with some detector/receiver technology. If the work progresses as planned, they will demonstrate open horizontal path measurements of CO<sub>2</sub> in the spring of 2002.

These scientists also offer the opinion that carbon dioxide measurements from several towers in or near the field, or from a small aircraft might be the most cost effective. Although space offers global coverage, it does so at the expense of a very long measurement range. That combined with the technical challenges of working for long periods in space make the space-based sensors and missions expensive.

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## APPENDIX B (continued) One Sheet Summaries for Selected NASA Project Areas

## APPENDIX C. DOCUMENTATION ABOUT VENDOR COMMERCIAL DETECTORS

Table C-1. Contact Information for Manufacturers and Vendors for Commercial Carbon Dioxide Monitors

Company	Contact Information	Company	Contact Information
AFC	PO Box 894	Air Instruments	13300 Brooks Dr # A
International,	Demotte, IN 46310	&	Baldwin Park, CA
Inc.	219-987-6825	Measurements,	91706
	219-987-6826 fax	Inc	626 813-1460
	www.afcintl.com		626 338-2585 fax
			www.aimanalysis.com
W.E. Kuriger	90 Atlantic Avenue	Li-Cor Inc	4421 Superior Street
Associates	Fitchburg, MA 01420		402-467-3576
	800 292-0921		www.licor.com
	978 342-5065 fax		
	www.airspill.com		
MSA	Instrument Division	RAE Systems,	1399 Moffett Park Dr.
Instruments	PO Box 427	Inc	Sunnyvale, CA 94089
	Pittsburgh, PA 15230		408 752-0723
	412-967-3228		408 752-0724 fax
	412-967-3373 fax		www.raesystems.com
	www.msanet.com		
RKI	1855 Whipple Road	Scott/Bacharach	251 Welsh Pool Road
Instruments	Hayward, CA 94544	Instruments,	Exton, PA 19341
	800 754-5165	LLC	610 363-5450
	510 441-5656		610 363-0167 fax
	510 441-5650 fax		www.baharach-eit.com
	www.rkiinstruments.com		
Sierra Monitor	1991 Tarob Court	SKC Inc.	863 Valley View Road
Corporation	Milpitas, CA 95035		Eighty Four, PA 15330
1	408 262-6611		724 941-9701
	800 727-4377		www.skcinc.com
	408 262-9042 fax		
	sierra@sierramonitor.com		
	www.sierramonitor.com		
Topac Inc.	99 Derby Street	Veris	503 598-4564
	Hingham, MA 02043	Industries, Inc	503 598-4664 fax
	781 740-8778		www.veris.com
	781 740-8779 fax		
	www.topac.com		

Table C-2 Commercial Fixed Point Carbon Dioxide Monitors

	Model	G 40 4	Approx.	
Manufacturer/Supplier	Number/Description	<b>Specifications</b>	<u>Price</u>	Comments
Air Instruments	8800 Series Open-			Available as
Measurements	Path Ambient Air			dispersive IR,
	Analyzer			UV, or a
				FTIR
				analyzer. IR
				is
				recommended
A : T	M - 1-1 7111 - 11-	0 10000		for CO <sub>2</sub>
Air Instruments	Model 7111 single	0 – 10000		NDIR (non-
Measurements	gas analyzer	ppm good to 1 ppm CO2		dispersive IR)
W.E.Kuriger	AirSense Model 310	0 - 2000  ppm	\$400 -	IR detection.
Associates	Sensor	+/- 5%	\$500	Diffusion or
		accuracy		duct sampling
W.E.Kuriger	Model 301A-1	0 - 2000  ppm	\$400 -	Smaller size
Associates	Carbon Dioxide	+/- 5%	\$500	version of
	Detector	accuracy		Model 310
MSA Instruments	Model 3600 Infrared	Available	\$1605	IR detection.
	Gas Monitor	ranges	Note is	Capable of
		0 to 0.2%	\$4065	remote
		$CO_2$	for	sampling
		0 to 1.0%	explosion	from 300 feet
		CO <sub>2</sub>	proof	
		0 to 5.0%		
250 4 7	7	CO <sub>2</sub>		
MSA Instruments	Model 3630 Infrared	Long term	Φ.7.2.0	IR detection.
	Gas Monitor	stability of	\$520	Designed
		+/5%		especially for
		0.45 0.20/ CO		indoor use.
		0 to 0.2% CO <sub>2</sub>		Capable of
				remote
				sampling from 300 feet
RKI Instruments	Spectralert D/DR	CO2 version:		Remote
KIXI IIISH UIIICIIIS	InfraRed Gas	0-2000, 5000,		sensor option
	Detector	10,000,		up to 50
	Detector	50,000 ppm		meters
		Accuracy +/-		Offshore
		2% fsd on all		stainless steel
		ranges		spec
				construction.
	<u> </u>	<u> </u>		construction.

Table C-2 Commercial Fixed Point Carbon Dioxide Monitors (continued)

	Model		Approx.	
Manufacturer/Supplier	Number/Description	<b>Specifications</b>	<u>Price</u>	<u>Comments</u>
RKI Instruments	Beacon 800 Model	Carbon		Permits from
		dioxide		one to eight
		Range 0 –	\$1995	sensor
		1.0%		transmitters.
				Beacon 800 can
				be wired to
				alarms, etc.
				Diffusion and
				sample draw
				heads available.
RKI Instruments	GD-K77D Series	Carbon		Electrochemical
	Smart	dioxide	\$1975	cell
	Sensor/Transmitter	Range 0 – 1.0		
	with Readout			
Scott/Bacharach	4679-IR GasPlus	0 - 2%, 0 -		Dual
	Carbon Dioxide Gas	5%		wavelength
	Transmitter	Repeatability	\$1632	detector, non-
		is +/- 2%		dispersive IR
		below 40%		(NDIR)
		full scale,		
		otherwise +/-		
		5%		
Scott/Bachrach	CO <sub>2</sub> Continuous	Available		Dual
	Monitor 2850	ranges		wavelength
		0 to 5.0% CO <sub>2</sub>		infrared carbon
				dioxide sensor
Sierra Monitor	Model 4102 Series	Accuracy of		Non-dispersive
Corporation	Carbon Dioxide	+/-5% of full	\$1100	IR (NDIR)
	Sensor Modules	scale	-	detection.
		4102-80 0-	\$1500	Diffusion gas
		2000		sampling.
		ppm		Models for wall
		4102-85 0-		mount and
		5000 ppm		locating in
		4102-86 0 –		ducts.
		20%		
		4102-89 0-		
		2000 ppm		

Table C-2 Commercial Fixed Point Carbon Dioxide Monitors (continued)

N. C. (G. 1)	Model N. 1	G .00 .10	Approx.	G .
Manufacturer/Supplier	Number/Description	<b>Specifications</b>	<u>Price</u>	Comments
Topac Instruments	Guardian plus CO <sub>2</sub>	Carbon		Special non
	Monitor	dioxide		dispersive
		Ranges 0 –	\$1700	dual
		3000ppm, 0 -		wavelength
		1%, 0 - 3%, 0		IR sensor.
		-5 %, 0 -		Remote
		10%		sensing
		Accuracy +/-		possible up
		2% of range		to 90 feet
				way.
Veris Industries, Inc.	CX Series CO <sub>2</sub>	Carbon		Dual
·	Sensors	dioxide	\$700 -	wavelength
		Range 0 –	\$850	detector,
		2000 ppm		non-
		Accuracy +/-		dispersive
		20 ppm		IR (NDIR)
		Range 0 –		, ,
		5000 ppm		
		Accuracy +/-		
		50 ppm		
Li-Cor	LI-800	Carbon	\$2550	Dual
		Dioxide		wavelength
		0 - 2000  ppm		detector,
		Accuracy +/-		non-
		2%		dispersive
				IR (NDIR)
Li-Cor	LI-62XX series	Accuracy to	\$8360	NDIR type;
		<1 ppmv		used in
		FF		aircraft
Li-Cor	LI-7500 Open Path	Accuracy to	\$12,900	12 cm open
	r	<1 ppmv	. ,-	path
	l .	- rr'	l	I

Table C-3 Commercial Portable Carbon Dioxide Monitors

	Model		Approx.	
Manufacturer/Supplier	Number/Description	<b>Specifications</b>	Price	Comments
AFC International	Series 2800 Carbon	0 - 50,000		IR detection.
	Dioxide Analyzer	ppm	\$940	Preset alarms
		Resolution		at 5,000 and
		100 ppm		10,000 ppm.
AFC International	Series 2810 Carbon	0 - 10,000		IR detection.
	Dioxide Analyzer	ppm	\$1210	Capable of
		Resolution		data storage
		100 ppm		
AFC International	Short Term (Draeger)	Various	Only a	Uses Draeger
	Tubes	ranges are	few	Tubes. Draw
		available	dollars	a sample by
			per	hand pump
			indicator	into indicator
			tube	tube. Color
				change
				indicates
				concentration
Rae Instruments	Gas Detection Tubes	Ranges	Only a	Uses Rae-
	and Pumps	300-5000 ppm	few	Sep Tubes.
		500-10000	dollars	Draw sample
		ppm	per	by hand
		2500-30000	indicator	pump into
		ppm	tube	tubes. Color
		5000 -		change
		100000 ppm		indicates carbon
Caatt/Daahanaah	Carbon Dioxide 2800	Danasa		dioxide level.
Scott/Bacharach	Carbon Dioxide 2800	Ranges 0 - 50000 ppm	\$914	Pump can draw
		Resolution	\$91 <del>4</del>	
		100 ppm		samples up to 125 feet
		100 ppiii		away. IR
				method for
				carbon
				dioxide
SKC Inc.	535 Carbon Dioxide	0 – 10000	\$495	Two channel
DIXC IIIC.	Monitor	0 = 10000   ppm	ΨΤͿͿ	IR
	1/10/11101	Accuracy +/1		absorption
		2%		principle
		2/0		principic

APPENDIX C. (continued)
INFORMATION ABOUT VENDOR COMMERCIAL CARBON
DIOXIDE DETECTORS