

**Carbon Dioxide Capture for Storage  
in Deep Geologic Formations –  
Results from the CO<sub>2</sub>  
Capture Project**

**Geologic Storage of Carbon Dioxide  
with Monitoring and Verification**

*Volume 2*

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# **Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO<sub>2</sub> Capture Project**

**Geologic Storage of Carbon Dioxide  
with Monitoring and Verification**

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## Chapter 20

# ATMOSPHERIC CO<sub>2</sub> MONITORING SYSTEMS

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### ABSTRACT

Monitoring for atmospheric CO<sub>2</sub> concentrations may be an integral part of any subsurface storage project. Several CO<sub>2</sub> measurement methods may be used to meet the monitoring objectives of (1) assuring there are no large leaks at the surface that might pose a health risk and (2) verifying that the injected CO<sub>2</sub> remains trapped below the Earth's surface.

Options include (1) remote sensing from satellites or aircraft, (2) open path instruments that can sample over significant distances and (3) a network of conventional fixed-point detectors. NASA indicates satellite surveys might be useful for a "global" view of CO<sub>2</sub>. Aircraft surveys may be a fast means to collect data near ground level, but this is only practical in an infrequent basis. Instruments located near ground level that are based on open path sampling may offer the most efficient means to monitor long term over a large surface area. They could have the capability to detect increases of just a few percent of CO<sub>2</sub> above normal background, over a sample path of tens of meters, and continuously with unattended operation. Many different commercial fixed-point units based on infrared (IR) spectroscopy are available. These detectors may be better suited to monitor sensitive, high-risk points of leakage rather than be deployed in a network to monitor large surface areas.

Besides reviewing atmospheric monitoring options, this chapter also quantifies the capability of ground-level instruments to identify leakages of carbon dioxide from the subsurface. In particular, the objective is to successfully detect the uniform leakage of as little as 1% of the total carbon dioxide injected into the subsurface over 100 years. This analysis suggests the local increased concentration of carbon dioxide into the atmosphere due to such a leak depends greatly on the leakage area, time duration, atmospheric conditions and proximity of the detector to the leak. In some scenarios such a leak would cause an increase of at least tens of ppmv of carbon dioxide in the near-surface atmosphere and likely would be detected by commercially available instruments as being above the natural background variations of carbon dioxide.

### INTRODUCTION

Desirable attributes for such monitoring tools include: (1) low cost, (2) accurate measurements of CO<sub>2</sub>, (3) measurement over a small as well a large surface area, (4) remote, automated, long-term operation, and (5) reliable and safe to use. One motivation for a monitoring program is to assure the public and the project employees that there are no very large gas releases that pose a risk to human health. A second concern is to locate quickly any smaller leaks that may compromise the permanent capture of the injected CO<sub>2</sub>.

Carbon dioxide is a relatively benign chemical, but at very high concentrations it does pose a risk. Atmospheric concentration of two percent carbon dioxide will cause a 50% increase in breathing rate; concentrations exceeding 1000 ppm (0.1%) cause noticeable symptoms in some people (drowsiness, headaches). The OSHA (Occupational Safety and Health Administration) maximum acceptable level is

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*Abbreviations:* CCP, carbon capture project; EOR, enhanced oil recovery; MCT, mercury cadmium tellurium (HgCdTe); TEC, thermal electric cooling.

5000 ppm. Because the natural background concentration of CO<sub>2</sub> is 300–400 ppmv in ambient air, one needs only to determine if there is a *very* significant increase before there are any human health concerns.

A complete surface monitoring program would consider several geographic scales:

- large areas—even beyond project boundaries—perhaps tens of square kilometers
- within project boundaries and at the “fence line”—cover several or more square kilometers
- 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.

Different monitoring “tools” will be required to fulfill all the measurement requirements. For very large areas, instrumentation mounted in satellite or low-flying aircraft could be a practical approach. Within a project area, sensors that can measure CO<sub>2</sub> over open path lengths of hundreds of meters 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 individuals to use when entering higher risk areas.

After reviewing different monitoring options, the latter portion of this chapter assesses the capability of ground-level instruments to successfully detect leakages of carbon dioxide. In particular, the focus is on whether ground-level instruments can detect leakage to the atmosphere of as little as 1% of the cumulative total of the carbon dioxide injected into the subsurface over a 100-year period (leakage of 0.01%/year for 100 years). The calculation methodology and results are presented below. Different anticipated scenarios for CO<sub>2</sub> leaks are considered (1) uniform CO<sub>2</sub> leakage over an area of multiple square kilometers, and (2) leakage from a point source.

## EXPERIMENTAL/STUDY METHODOLOGY

### *Literature Review*

This effort uses information from the open literature, plus contacting NASA and industrial sources.

### *Capability of Ground-Based Instruments to Measure Carbon Dioxide*

Based on instrument specifications and making key assumptions concerning the storage project operation (such as the source of leak, detector location, weather conditions, variations in background concentrations, etc.), one can calculate whether a particular instrument package would successfully identify that leak of carbon dioxide.

### *Leakage over a wide surface area*

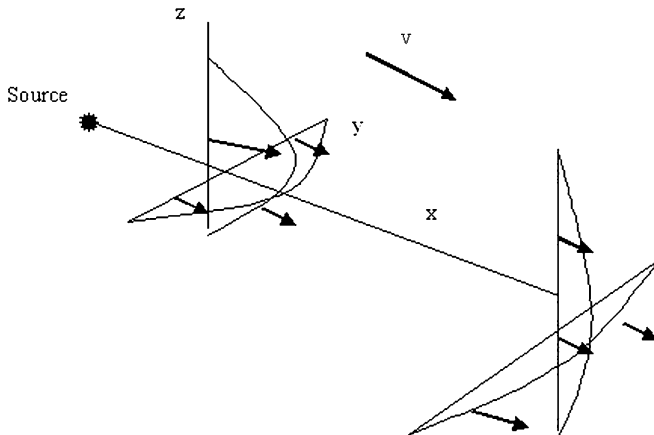
From the following sequence of calculations one can estimate the increase in CO<sub>2</sub> concentration to the atmosphere (near ground level) from leakages over a relatively large surface area. These include (1) compute the total mass of CO<sub>2</sub> injected, (2) assume some percent of this gas leaks to the surface (default is 1% of total injected), (3) input the surface area and duration of time of the leak (determines a flux of CO<sub>2</sub>), (4) calculate the volume of an imaginary “box” near ground level where the sensor is located—use a height of 3.3 m (10 ft)—and calculate the mass of CO<sub>2</sub> added to this volume daily, and (5) include a dilution factor to account for atmospheric conditions that would deplete the added carbon dioxide to this “box” volume.

The next step is to compare the calculated increase of CO<sub>2</sub> concentration to the two main uncertainties in the measurement: (1) the uncertainty of the instrument measurement, and (2) the natural variation in the background CO<sub>2</sub> concentration. For the former uncertainty, one may consult the detector performance for the selected instrument, plus one must pay attention to proper calibration of any instrument. For the latter uncertainty factor, the natural variation of CO<sub>2</sub> would depend on the sampling location and time of year (or even time of day). The atmospheric CO<sub>2</sub> concentration near the ground can be significantly affected by fluxes of CO<sub>2</sub> with terrestrial vegetation, types of soils, subsurface moisture, and water bodies. Diurnal and seasonal variations of several ppm or more are typical above a vegetated land surface. For example, Conway [1] reports a monthly variation of approximately 5 ppmv CO<sub>2</sub> at one fixed location. Even without local fluxes, the background CO<sub>2</sub> concentration varies significantly and on a range of timescales, as a result

of natural and industrial fluxes. The annual average carbon dioxide concentration also has been increasing about  $0.5 \pm 0.3\%$ , adding to the background levels. If the actual increase in  $\text{CO}_2$  concentration is substantially greater than all these uncertainties, the instrument measurement will recognize that there is a leak.

#### *Leakage from a point source*

The second type of calculation considers if instead the leakage is described better as a point source (e.g. leaks from around a wellbore) instead of a uniform leakage over a significant surface area. We use a simplified approach of a Gaussian distribution analysis to illustrate the general procedure to analyze the situation where the gas is venting to the surface at a single spot [2,3]. Figure 1 shows a sketch of the problem we are considering, the dispersion of this contaminant plume.



**Figure 1:** Schematic of movement of a plume of carbon dioxide coming from a point source and depleting in concentration as it moves downwind.

$$\text{Conc}(x) = Q/(\pi\sigma_y\sigma_z u)$$

where  $\text{Conc}(x)$  is the concentration of added  $\text{CO}_2$  at ground level, center of the plume;  $Q$  the uniform emission rate of carbon dioxide (g/s);  $\sigma_y$  the standard deviation of plume concentration distribution, horizontal direction (m);  $\sigma_z$  the standard deviation of plume concentration distribution, vertical direction (m) and  $u$  the mean wind speed affecting the plume (m/s).

The plume spread has a Gaussian distribution in the horizontal and vertical planes. The calculated concentration is for the additional  $\text{CO}_2$  concentration (in excess of the local background level) that is in the center line, downwind of the source. To use this equation (1) input the total mass of  $\text{CO}_2$  injected and the percent assumed to leak, (2) choose a time duration for the leak, (3) specify a wind speed, and (4) estimate the horizontal and vertical dispersion coefficients. This last step becomes somewhat involved as it requires referring to tables and graphs. First, one needs to select the atmospheric conditions, done via the so-called Pasquill Stability Class, as described in Table 1. The stability classification ranges from A through F, based on wind speed, time of day, and the degree of overcast. Next, one refers to graphs to determine the horizontal and vertical dispersion coefficients (Figures 2 and 3).

More recent models of pollution dispersion have advanced beyond the Gaussian model and Pasquill Stability Classes utilized here. These more sophisticated models would be appropriate to forecast and analyze leakage behavior for specific storage projects where one would want to account for the local

TABLE 1  
PASQUILL STABILITY CLASSIFICATIONS

Pasquill Stability Classes  
 A: Extremely unstable conditions  
 B: Moderately unstable conditions  
 C: Slightly unstable conditions  
 D: Neutral conditions  
 E: Slightly stable conditions  
 F: Moderately stable conditions  
 G: Extremely stable

Meteorological conditions defining Pasquill Stability Classes

Surface wind speed (m/s)	Daytime insolation			Night-time conditions	
	Strong	Moderate	Slight	Thin overcast or >4/8 low cloud	≤ 4/8 cloudiness
<2	A	A-B	B		
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
>6	C	D	D	D	D

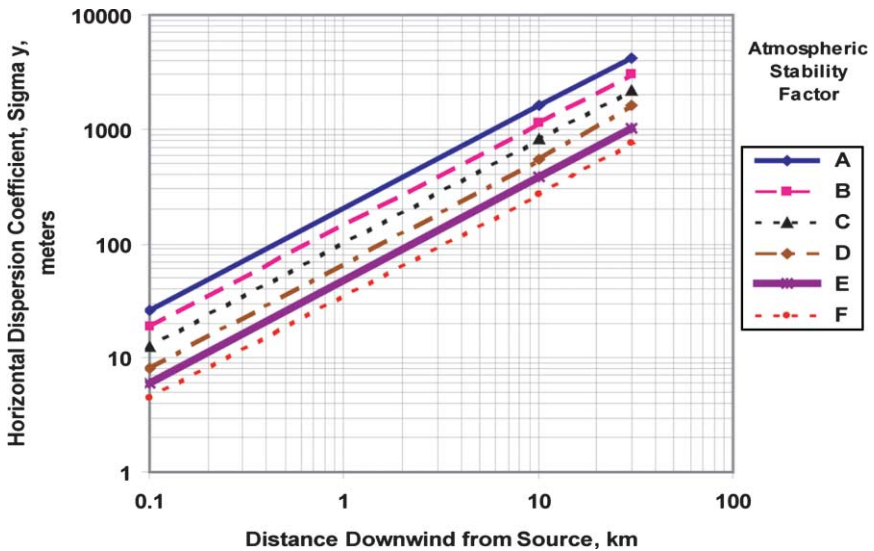
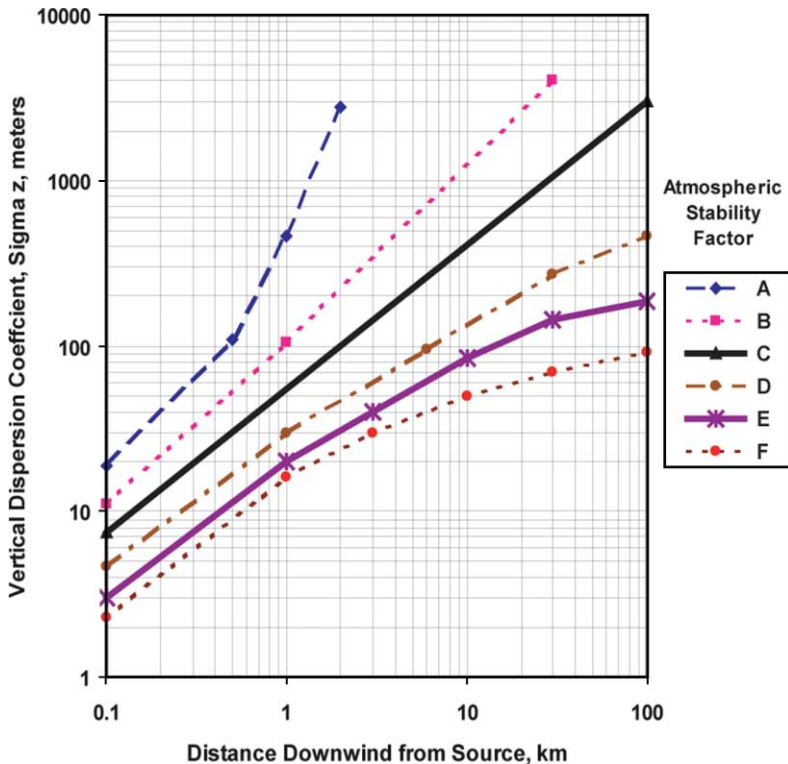


Figure 2: Horizontal standard deviation, dispersion factor, versus the distance downwind from the point source for different atmospheric conditions.





**Figure 3:** Vertical standard deviation, dispersion factor, versus the distance downwind from the point source, for different atmospheric conditions.

topography and other site-specific details. Newer analytical techniques take into account more fully the physical processes and structure of the atmosphere, while even more sophisticated models incorporate actual topography and dynamic meteorology. Some atmospheric models are offered as packages with license fees, others as shareware. Some of these models are endorsed by regulatory bodies such as environment protection authorities.

## RESULTS AND DISCUSSION

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

See Table 2.

#### *Infrared analysis—general background*

Although there are number of different approaches for CO<sub>2</sub> measurement in the ambient air, variations of infrared (IR) detection is the most common technique. CO<sub>2</sub> has unique absorption bands in the IR. Table 3 lists the absorption strength at different CO<sub>2</sub> bands. IR analysis in the open air can measure directly the bulk CO<sub>2</sub> concentration.

The band chosen for CO<sub>2</sub> analysis is based on its absorption strength and the potential interferences from other gases. High absorption bands (such as at 4.25  $\mu$ ) can detect very low concentrations of CO<sub>2</sub> over even a short sample path length. Most fixed and portable commercial CO<sub>2</sub> monitoring systems are based on IR

TABLE 2  
COMPARISON OF METHODS FOR MEASUREMENT OF ATMOSPHERIC CARBON DIOXIDE

Measurement type	Description (application)	Sensitivity/cost for ambient air sampling	Advantages	Disadvantages
Satellite	Remote sensing (potential to cover hundreds of square miles/survey; for infrequent large area sampling)	Costs can be of the order of $\$10^4$ – $\$10^5$ per survey. NASA claims can resolve to 100 ft <sup>2</sup> Hyperspectral survey can resolve to a few meters	Covers very large area  Technology development sponsored at least in part by the government	Only a “2D view”, not sample at ground level for direct CO <sub>2</sub> measurement Available satellites might not cover project area
Airborne	Remote sensing (potential to cover tens to hundreds of square miles; for infrequent sampling)	Estimated at \$100 per survey Single measurement to 3% ±	Cover large area Fairly fast over tens of square miles	Only practical for occasional “snapshot” surveys
Open path laser spectrometer	Ground level (potential to cover several square miles with one device; can be main instrument for long-term monitoring)	Estimated \$1000 per unit Instrument needs development, but estimate can be 3% ± or better	Potential for one fixed instrument to cover large area Measurement could be automated, continuous	Technology for long, open light path detection is still under development
Fixed-point detectors	Ground level (sample at single fixed points of high risk of leaks)	Fairly cheap (circa \$1000) Routinely better than 3% ± . Less than 1% ± available	Fairly cheap and proven technology Best used as points of higher risk	Only measure CO <sub>2</sub> at the detector location Require multiple sensors to sample even a small area
Portable detectors	Personal protection and scan for equipment leaks	Very cheap; units can cost <\$500 Better than 5% ±	Very cheap; can move to suspect “hot spots”	Only suitable for spot checking CO <sub>2</sub> concentrations

TABLE 3  
WAVELENGTHS FOR CARBON DIOXIDE ABSORPTION

Wavelength ( $\mu\text{m}$ )	Relative absorption strength
1.432	1
1.570	3.7
2.004	243
2.779	6800
4.255	69,000

absorption at 4.25  $\mu$  and use a very short optical path at this band along with a filament light source. Usually, the absorption of IR light passing through a confined gas cell is measured. The light is normally generated with a metal filament, giving out radiation from 3 to 10  $\mu$  and a power of several microwatts and filtered to 4.25  $\mu$ . The detector often is an MCT (Mercury Cadmium Tellurium, HgCdTe) detector with TEC (Thermal Electric Cooling). Such highly absorbing 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<sub>2</sub> are more suitable for measuring high concentrations of CO<sub>2</sub> or to measure its concentration over a long path length.

The second strongest absorption band by CO<sub>2</sub> is around 2.7  $\mu$ ; the relative absorption strength here is about 1/10th of the absorption strength at 4.25  $\mu$ . This band is also very sensitive and relatively free of interference from other gases. It has been used, e.g. to measure CO<sub>2</sub> levels by the Mars Explorer by NASA. However, there are no commercial diode lasers for this band and NASA had to develop a custom laser. Its relatively strong absorption also does not allow this band to be used for CO<sub>2</sub> detection over a long beam path either.

One other band is the 4.41  $\sim$  4.45  $\mu$  band, which is the absorption band for <sup>13</sup>C CO<sub>2</sub>. Because <sup>13</sup>C occurs at a much lower level than <sup>12</sup>C (about 1/100th as much), this band allows detection of much higher level of total CO<sub>2</sub>. 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.

Another potential band is the 2  $\mu$  band, with the absorption strength for CO<sub>2</sub> being at least 250 times weaker than at 4.25  $\mu$ . The interferences of other gases are also much weaker than CO<sub>2</sub> if a narrow light source is used as the probe. This weak absorption band has already been used for detection of CO<sub>2</sub> in combustion environment [4]. One advantage of this wavelength is the availability of lower cost diode lasers with very narrow (0.01 cm<sup>-1</sup>) bandwidth at this band. Another advantage is the availability of InGaAs detectors with much better signal-to-noise ratio compared to MCT (HgCdTe) detectors used for 4.25  $\mu$ . Based on the absorption strength of CO<sub>2</sub> at this band, in theory, one can measure CO<sub>2</sub> concentration as high as 0.5% over a path length distance of 200 m.

There is a third band at 1.57  $\mu$  for the adsorption of CO<sub>2</sub>'s overtone. The absorption by CO<sub>2</sub> at this band is much weaker (close to 1/100) than the band at 2.01  $\mu$ , and is only 1/20,000th compared to the absorption at 4.25  $\mu$ . This band is almost completely free of interference by other gases. This band has been investigated as a means for CO<sub>2</sub> detection in a combustion chamber [5]. They found the band to be free of interference from other gases, but it is too weak for short path detection of CO<sub>2</sub>. However, this wavelength should be well suited for long path CO<sub>2</sub> detection at concentrations typical of ambient air. 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. The band at 1.43  $\mu$  is even weaker. Because water absorption is significant at this wavelength, this is not appropriate for detection of CO<sub>2</sub> 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 distance. If there is further modification that the instrument can rotate and reflect a signal from multiple retro-reflectors, then a single laser could sample out several direction and distances and thereby sample an area of the order of a square kilometer. 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<sub>2</sub> concentrations over a small portion of the light path. Hence, if this device measures a significant increase in CO<sub>2</sub> concentrations, one would have to sample further in the suspicious area with perhaps a portable unit to pinpoint the source(s) of the elevated CO<sub>2</sub> in that sampling path.

After reaching the 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. 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 detector falls to the same level as noise. Based on this result, one should be able to probe CO<sub>2</sub> concentration up to 360 ppm over a distance of 15 m range by concentration product of 5400 m ppm.

One could select other wavelengths for performing the measurement where the CO<sub>2</sub> absorption is even 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 ca. 360 ppm. For example, for the band at 1.57 μ where the absorption by CO<sub>2</sub> is much weaker (only 1/20,000th compared to that for 4.25 μ), one could in theory detect up to 1% of CO<sub>2</sub> over a light path as long as 1 km.

The cost for an open path instrument is about \$50,000, and a whole detector system with multiple retro-reflectors could be as much as \$150,000 [6]. Another vendor provides a cost estimate of about \$50,000/month to conduct a full-service detailed study of a point source problem (e.g. fumes from a dump site, see Ref. [7]). The design of a similar open-path instrument, but specifically designed only for duty as a carbon dioxide detector at storage sites may result in a less costly version of the technology. For carbon dioxide, the common approach for single point detectors is to use the very strong IR absorption band at 4.2 μm. For application as an open path detector, it is recommended that the wavelength of 1.57 ~ 1.60 μm be used. At this wavelength the absorption for carbon dioxide is quite low and largely free of interferences such as water vapor. With recent technology advances in the telecom and other electronic industries, it is conceivable that off-the-shelf parts could be assembled to build such a lower cost open-path instrument.

#### *Solid-state chemical sensors*

Based on the ionic reaction of  $A^+ + OH^- + CO_2 = AHCO_3$  (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 100 ppmv to 5 vol.%. But, it is subject to water condensation and therefore not reliable [8–10]. For example, the reading of potential changed by as much as 25% when the water concentration goes up from 0.7 to 30 vol.% [8].

Based on 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 nanocrystalline materials [9]. 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 nanocrystalline material changed its structure after several days, degrading sensitivity [9]. Micromechanical detectors sense 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 [10]. All the above chemical solid-state sensors could be made into very small inexpensive packages, but each sensor could only measure CO<sub>2</sub> at a single point.

#### *Gas chromatography*

Carbon dioxide may be measured easily to within a few ppm by standard gas chromatography methods. This is not used very much currently for atmospheric analysis, but it is a standard method for indoor air quality. OSHA uses this as a benchmark to compare against other proposed measurement techniques. Their concern

of course is to determine worker exposure to CO<sub>2</sub>. For more details, see, e.g. <http://www.osha-slc.gov/dts/sltc/methods/inorganic/id172/id172.html>.

#### *Chemical reaction/visual indication*

Another 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<sub>2</sub> brought in to create a color change. The concentration of CO<sub>2</sub> may be read from the length of the stain. These tubes come in a variety of concentration ranges in order to improve the accuracy of the measurement. The cost of each disposable tube is a few dollars.

### **CO<sub>2</sub> MONITORING PROGRAMS IN CURRENT SUBSURFACE (EOR) GAS INJECTION PROJECTS**

Several operators of ongoing CO<sub>2</sub> injection projects were contacted for comments concerning current practices to monitor for atmospheric carbon dioxide concentrations. 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 H<sub>2</sub>S is present in the gas streams along with the carbon dioxide, emphasis is placed on monitoring and preventing human exposure to leakages of the much more dangerous hydrogen sulfide. For example, at Chevron’s Rangely Field in Colorado and Kinder Morgan’s EOR project in Snyder, Texas, the operators are aggressive in guaranteeing that no person is exposed to even small releases of H<sub>2</sub>S gas. Engineers we contacted at these companies said that state-of-the-art (a sensitive gas detector, remote data acquisition, and alarm system) H<sub>2</sub>S detection schemes have been placed at selected critical points, with each unit costing of the order of \$3000/installation.

These operators said there were minimal legal requirements for monitoring of CO<sub>2</sub> gas as it is considered a non-toxic substance. One engineer contacted at Kinder Morgan, a major producer of CO<sub>2</sub>, said 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 indirect indicators of pipeline leaks such as changes in flow and pressure readings. New CO<sub>2</sub> subsurface injection projects where the main motivation is for storage have paid more attention to monitoring issues, particularly measurements to detect the subsurface migration of injected carbon dioxide.

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

Key NASA projects concerning carbon dioxide monitoring have been focused at three NASA sites (JPL—Jet Propulsion Laboratory/Pasadena, CA; Langely/Hampton, VA; and Goddard Space Flight Center/Greenbelt, MD). 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 monitoring CO<sub>2</sub> concentrations at carbon storage 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, one project sponsored by the CCP investigated this concept [11]. Another indirect approach is remote surveys for detecting subtle changes in the surface deformation. These changes reflect movement of pressure changes subsurface associated with CO<sub>2</sub> injection [12].

One common opinion 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 [13,14]. One can resolve carbon dioxide concentrations in blocks perhaps as small as 100 m<sup>2</sup>. 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 third, vertical dimension, and focus their detection to just near ground level, which is of primary interest to this application. Increases in near-surface CO<sub>2</sub> levels due to leakage of injected gas might be detected, but increases in CO<sub>2</sub> in the upper atmosphere for other reasons

also would be detected. That is, this approach might be subject to “false positives”. Thus satellites might be a good tool as a “screening” method to spot unusual changes in CO<sub>2</sub> levels; but those changes may not necessarily be at ground level nor related to activity at the storage 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 aircraft surveys are an alternative movable platform for more detailed remote measurement over a near ground-level carbon dioxide concentration. One can choose the exact area to perform such a survey, but the cost and logistics may make this impractical for frequent sampling.

As expected, NASA has its focus on interplanetary space exploration and high atmospheric research for Earth [14–16]. While perhaps not directly applicable for storage monitoring goals, improved laser detection and associated measurement research at NASA could prove useful. For example, projected research at JPL includes development of a superior InGaAsSb/GaSb laser that can detect spectra 2–5  $\mu$ . Intersubband Quantum Cascade lasers are being developed for Mars exploration. The wavelengths are in the range of 4–11  $\mu$ , typically with a power of 10–20 mW.

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

There are a number of commercially manufactured carbon dioxide detectors. Typically the detector itself is an NDIR (non-dispersive IR) type. The cost of just the detector can be less than \$1000. Adding a visual readout or rudimentary data acquisition capability can increase the price to as much as \$2000. A full gas sensor system rated as explosion proof can approach \$4000 per installation. Most of these devices are intended as room gas monitors.

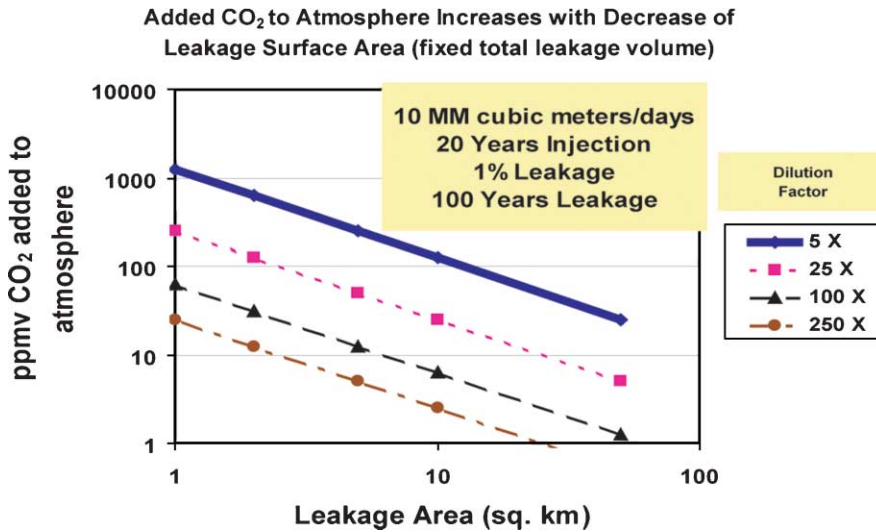
Advantages of these instruments are that they are relatively low cost and can indicate at least any large shift in the atmospheric CO<sub>2</sub> concentration. Their responses to changes in the CO<sub>2</sub> concentration are no more than a few seconds, and they have the capability to provide a continuous read out of results. A major limitation of these devices is that typically they will sample the atmospheric gases at one fixed point. Thus a great many commercial sensors would be required in order to cover a substantial area. This means the associated cost to collect the data in this network, plus process all the data, increases rapidly as the number of fixed sensors and the area covered increases. These associated installation costs likely would exceed the cost of the individual detectors.

The claimed accuracy of these instruments varies significantly. Some of the low-cost devices (around \$500) are accurate to only  $\pm 5\%$  of full scale. Other vendors claim their instruments can achieve an accuracy of  $\pm 2\%$ , or better. More expensive ones are accurate to  $\pm 1\%$ , and one vendor claims an accuracy to 1 ppm or better.

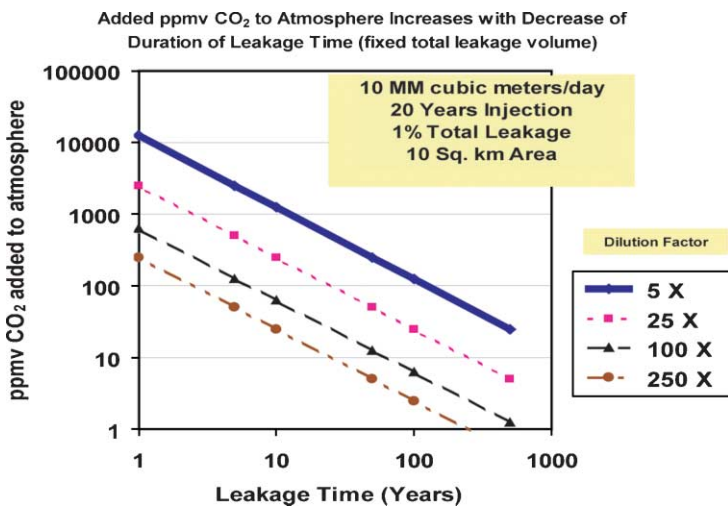
Portable (hand-held) detectors are appropriate for personal protection as there is some mild health concern with people being exposed to high levels of carbon dioxide gas. Workers who are in the project area on a regular basis should have access to devices before entering any higher risk area. The resolution of these devices is typically no better than 100 ppm. This is sufficient accuracy if the main purpose is just to verify that the local CO<sub>2</sub> concentration does not pose a health concern. These portable meters commonly are less than \$1000 each, and most use IR detection.

#### ***Quantitative Analysis of Capabilities for Detecting CO<sub>2</sub> in Ambient Air***

First, consider the scenario where the carbon dioxide leak occurs uniformly over a substantial area (say over a square kilometer or more). The graphs below illustrate changes that would occur in the added concentration of carbon dioxide to the background levels, under different assumptions. These calculations presume gas injection for 20 years at a rate of 10 million cubic meters/day (basis of 1 atm and 15 °C), and that 1% of that total injection gas then does leak. Figures 4 and 5 illustrate that either decreasing the surface area or the time duration over which the leakage of carbon dioxide occurs increases its concentration near ground level.

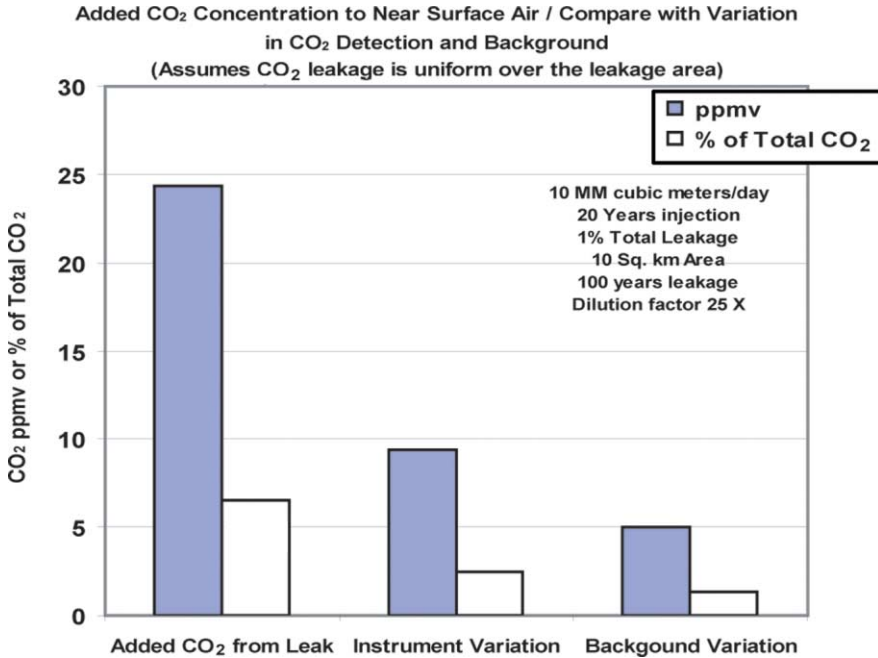


**Figure 4:** Example calculation results illustrating that the added carbon dioxide concentration to the near ground-level atmosphere increases with a decrease in the leakage area.



**Figure 5:** Example calculation results illustrating that the added carbon dioxide concentration to the near ground level atmosphere increases with a decrease in the leakage time.

It is not surprising from the above graphs that there are scenarios where the local addition of CO<sub>2</sub> either may or may not be easily detectable. For example, Figure 6 illustrates a scenario where the local additional CO<sub>2</sub> concentration approaches 25 ppmv. This is substantially greater than the uncertainty associated with variations in the background and measurement fluctuations in this illustration. The next example (Figure 7) is a contrary case where the increase in added CO<sub>2</sub> concentration would be difficult to detect as it is no more than the measurement uncertainties.

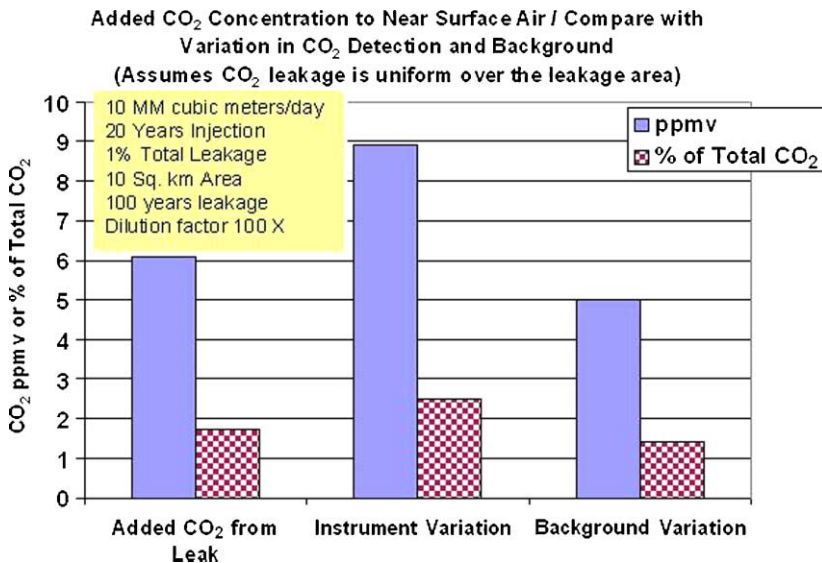


**Figure 6:** Example calculation result illustrating a scenario where the increase in the carbon dioxide concentration from a leak is substantially above the uncertainties of the measurement and the background concentrations.

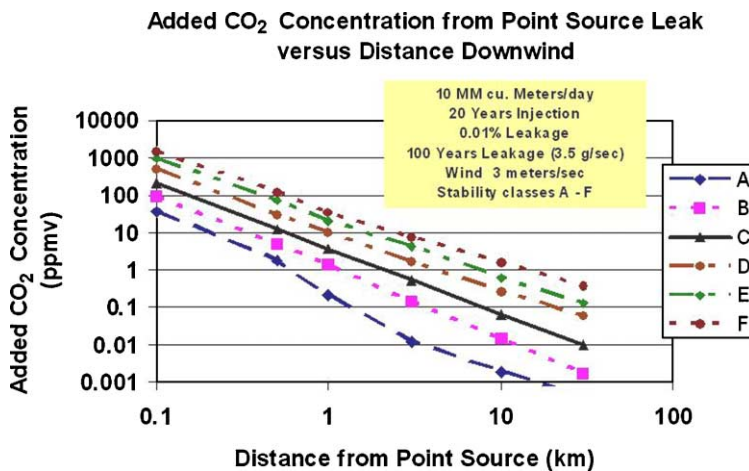
One way to improve this detection limit is to reduce the uncertainty in the background noise. This could be accomplished by careful, extensive background measurements of carbon dioxide before gas injection over time periods of hours, days, weeks, or even months (interannual differences can be large). Incorporating the measurements methods detailed here, vertical profiles of CO<sub>2</sub> from towers combined with micrometeorological techniques could be used to determine CO<sub>2</sub> fluxes. Some of the established measurement network stations could be of useful (e.g. the Global Atmospheric Watch network of the World Meteorological Organization, the Fluxnet flux stations). From such careful background data one could quantify better and account for this source of uncertainty. In any case, it is good engineering practice to establish the background responses of the instrument package under field conditions selected before the initiation of carbon dioxide injection. Another tact is to select a detector to improve the accuracy of the measurement.

The other scenario considered is when the leak occurs at a point. Examples include a localized leak with gas coming up a wellbore or leaks from a piece of faulty surface equipment. Figures 8 and 9 are calculated results of the profile of CO<sub>2</sub> concentration from point source leaks versus the distance away, directly downwind. These examples show a very wide range of responses. Note that Figure 8 considers the case

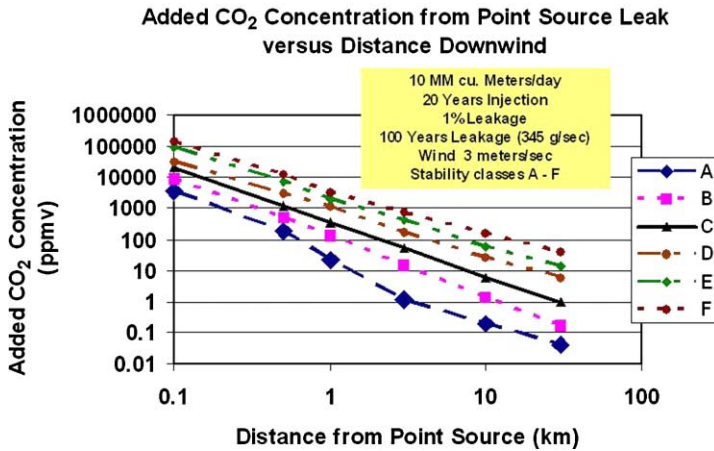




**Figure 7:** Example calculation result illustrating a scenario where the increase in the carbon dioxide concentration from a leak is substantially below the uncertainties of the measurement and the background concentrations.



**Figure 8:** Example calculation result illustrating the decrease in the concentration of CO<sub>2</sub> versus the distance downwind. Results are shown for different atmospheric stability conditions and for a leakage of 0.01% of injected carbon dioxide over a 100 year period.



**Figure 9:** Example calculation result illustrating the decrease in the concentration of CO<sub>2</sub> versus the distance downwind. Results are shown for different atmospheric stability conditions and a leakage of 1% of injected carbon dioxide over 100 years.

where the CO<sub>2</sub> leakage is 0.01% of the total injected CO<sub>2</sub>. In contrast, Figure 9 presents similar calculations, but now for the scenario of 1% of the total injected gas escapes at a single point leak over 100 years. Not surprisingly, the concentration of *added* CO<sub>2</sub> (above the background level) versus distance from the point source is much greater for the latter case with the 100-fold greater leakage rate. In both figures we show that the atmospheric conditions can have a substantial effect. As expected, as one increases the stability of the atmospheric conditions, the increase in CO<sub>2</sub> centerline concentration increases.

Table 4 below compares the distance from the point source of the leakage where the concentration of the added carbon dioxide falls to 10 ppmv. At these distances and closer, CO<sub>2</sub> concentrations are high enough so it is likely that many commercial detectors located downwind would determine there is a leak. These results emphasize changing the atmospheric conditions causes a wide variation in the calculated results. At one extreme of a relatively small leak and unstable atmospheric conditions, the distance is significantly less than a kilometer. At the other extreme of a large point leak scenario and stable atmospheric conditions, the concentration of added carbon dioxide can persist above 10 ppmv for several kilometers.

TABLE 4  
DISTANCE (KM) DOWNWIND OF A POINT SOURCE OF CARBON DIOXIDE LEAKAGE WHERE  
ADDED CONCENTRATION FALLS TO 10 PPMV FOR DIFFERENT DISCHARGE RATES

		Pasquill stability class					
Percent of injected	Leakage rate (g/s)	A (km)	B (km)	C (km)	D (km)	E (km)	F (km)
0.01	3.5	0.2	0.35	0.5	1	1.7	2.3
0.1	34.5	0.7	1.3	2.5	5	7.5	15
1	345	1.2	3	8	22	37	80

## CONCLUSIONS

From this literature review we conclude the following.

1. A suite of different types of CO<sub>2</sub> detection methods are available to acquire atmospheric data to verify the integrity of a subsurface injection project from small to large area.
2. A newer concept for ground-level measurement of carbon dioxide measurement is to use an open-path instrument. These detectors respond to the CO<sub>2</sub> concentration, averaged over the entire sample path length. With this arrangement, a single laser instrument could sample several directions, thereby covering a wide area. This concept could be more efficient than using a large network of commercial, single-point detectors to measure carbon dioxide concentration at ground level over a large storage project area. Existing open path instruments are relatively expensive, but costs might be reduced if a customized device is constructed that only need measure carbon dioxide.
3. Regarding the calculations of required performance of ground-level instruments to identify leakages from the subsurface:
  - Key factors that determine the increase in the ground-level carbon dioxide concentrations include (1) the total mass amount of CO<sub>2</sub> leakage, (2) the leakage surface area and duration of the event, and (3) atmospheric effects that dilute the influx of added CO<sub>2</sub>.
  - Calculations suggest a leakage of just 1% of the total carbon dioxide injected could add tens of ppmv of this gas to the local air environment if the leak occurs uniformly over a few square kilometers or smaller area and/or in a time period of several months or shorter. Such leaks would be identified if the detector is in close proximity.
  - For leakages emanating from a point source, the CO<sub>2</sub> concentration downwind of the leak increases with an increase in the (1) mass rate of discharge, (2) stability of atmospheric conditions, and (3) proximity of the sensor to the leak. Example calculations illustrate the atmospheric conditions alone can change by an order of magnitude the distance from which a sensor can recognize a leak is occurring.

## RECOMMENDATIONS

Development should be encouraged for less expensive long, open-path instruments to measure CO<sub>2</sub> in the ambient air. Potentially, a single such laser device could sample a radius of several square kilometers. 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.

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 geologic storage.

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.

Use ongoing CO<sub>2</sub> storage project sites and oil field injecting CO<sub>2</sub> for EOR as test beds to evaluate and further develop these CO<sub>2</sub> monitoring concepts. Also natural sites where there are elevated CO<sub>2</sub> concentrations (e.g. volcanic activity) are candidate field evaluation sites.

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 storage projects.

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## REFERENCES

1. T.J. Conway, P.P. Tans, L.S. Waterman, K.W. Thoning, D.R. Kitzis, K.A. Masarie, and N. Zhang, *J. Geophys. Res.* **99D** (1994) 22831–22855.
2. Workbook of Atmospheric Dispersion Estimates, from EPA, web site: <http://www.waketech.edu/math/projects/Weston/Dispersion.htm>.
3. Air Pollution Workbook, Atmospheric rate modeling, web site: <http://homepages.utoledo.edu/aprg/courses/iap/TEXT/workbook/chap4.html>.
4. M.E. Webber, S. Kim, S.T. Sanders, D.S. Baer, R.K. Hanson, Y. Ikeda, *Appl. Optics* **40** (6) (2001) 821–828.
5. D.M. Sonnenfroh, M.G. Allen, *Appl. Optics* **36** (15) (1997) 3298–3300.
6. E. Thornton, N. Bowmar, The application of a laser based open-path spectrometer for the measurement of fugitive emissions and process control, presented at A&WM Association Conference, Raleigh, NC, 28 October, 1999.
7. Minnich and Scotto, web site: use of open-path FTIR spectroscopy during site remediation, [www.msiar.net/openpathspec.html](http://www.msiar.net/openpathspec.html).
8. N. Imanaka, *Sensor. Actuat. B-Chem.* **24** (1995) 380–382.
9. P. Kellera, H. Ferkelb, K. Zweiackera, J. Naserb, J.-U. Meyera, and W. Richemannb, *Sensor Actuat B-Chem.* **57** (1–3) (1999) 39–46.
10. Q.Y. Cai, A. Cammers-Goodwin, C.A. Grimes, *J. Environ. Monitoring* **2** (6) (2000) 556–560.
11. W.L. Pickles, Geobotanical hyperspectral remote sensing, presented at the *CCP Carbon Sequestration Conference*, Potsdam, Germany, 30 October–1 November, 2001.
12. H.A. Zebker, J. Harris, Monitoring the injection and storage of CO<sub>2</sub> using satellite radar interferometry, presented at the *CCP Carbon Sequestration Conference*, Potsdam, Germany, 30 October–1 November, 2001.
13. Abshire, James, Personal Communication, NASA, Goddard Space Center, Space Born Laser Development.
14. R.W. Carlson, A tenuous carbon dioxide atmosphere on Jupiter's moon Callisto, JPL Report, 3 November, 1998.
15. G. Vane, Airborne visible/infrared imaging spectrometer (AVIRIS), JPL Publication 87-38, 15 November, 1987.
16. M.A. Vincent, S.S. Saatchi, Comparison of remote sensing techniques for measuring carbon sequestration, JPL Publication, February, 1999.