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Studying the vegetation response to simulated leakage of sequestered CO_2 using spectral vegetation indices

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ABSTRACT

Measurement of spectral reflectance provides a fast and nondestructive method of stress detection in vegetation. In this shallow subsurface CO_2 release experiment to simulate CO_2 leakage of geologically sequestered CO_2, the radiometric responses of plants to elevated soil CO_2 concentration were monitored using a spectroradiometer. Spectral responses included increased reflectance in the visible spectral region and decreased reflectance in the near-infrared region and thus an altered spectral pattern of vegetation. Visible responses of vegetation include purple discoloration and eventual death of leaves at sites where the soil CO_2 concentration was very high. Derivative analysis identified two features (minimum and maximum) in the 575–580 nm and 720–723 nm spectral regions. The normalized difference first derivative index (NFDI) was defined based on the spectral derivative at the two bands. Four vegetation indices were analyzed with the accumulated soil CO_2 concentration to assess the accumulated impact of high soil CO_2 concentration on vegetation. Results show that with increased soil CO_2 concentration due to the surface CO_2 leakage, (1) the structural independent pigment index (SIPI) increased, indicating a high carotenoid to chlorophyll ratio; (2) the chlorophyll normalized difference vegetation index (Chl NDI) decreased, suggesting a decrease in chlorophyll content with time; (3) pigment specific simple ratios (both PSSR*a* and PSSR*b*) were reduced for stressed vegetation compared to that at the control site, indicating a reduction in both chlorophyll *a* and chlorophyll *b*; and (4) NFDI was low where plants were stressed. Changes in NFDI during the experiment were 36% and 1% for stressed and control plants, respectively. All four indices were found to be sensitive to stress in vegetation induced by high soil CO_2 concentration.

1. Introduction

One of the potential options to mitigate the contribution of fossil fuel emissions to the global warming problem is to capture and store CO_2 in deep geological formations such as depleted oil and gas fields, unminable coal beds, and deep saline formations (IPCC, 2005). However, associated with the safety of CO_2 storage, the extent of CO_2 leakage is one of the key questions related to the integrity of storage (Hepple and Benson, 2005). Leakage of sequestered CO_2 adds one more potential source of CO_2 leakage to the atmosphere (Holloway, 2005), along with various other biogenic and geological sources. It is imperative to ensure the safe storage of CO_2 underground by developing monitoring techniques.

As CO_2 seeps to the ground surface, it could deplete oxygen in the soil atmosphere and could cause stress in the local vegetation. The primary cause of the stress, in response to natural gas leaks, is believed to be displacement of oxygen from the soil atmosphere, which thereby inhibits root respiration that provides energy for root growth and uptake of nutrients from the soil (Hoeks, 1972a; Gilman et al., 1982; Arthur et al., 1985). Displacement of soil oxygen has negative effects on plant growth which are expressed as reduced root and shoot growth and reduced dry weight (Drew, 1991). For instance, Noomen and Skidmore (2009) found that increasing soil CO_2 concentrations decreased plant height, leaf chlorophyll content and dry weight of maize plants. Boru et al. (2003) reported that a 50% CO_2 concentration at the root zone has shown either death of soybean plants or severe symptoms of chlorosis, necrosis and root death. Compromise to the health of plants due to stress is often associated with an increase in spectral reflectance in the visible region and a decrease in the near-infrared (NIR) region. This results in a shift of the slope between red and NIR, called 'red-edge position', towards shorter

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wavelengths. Since it is known that the changes in spectral reflectance are often a stress induced response of plants (Macek et al., 2005; De Jong, 1998), these changes in spectral reflectance could be used as a proxy indicator of CO_2 leakage.

Hyperspectral remote sensing (HRS) is a useful method to monitor spectral changes in vegetation. HRS contains significant spectral information for detecting plant stress (Carter, 1994; Carter, 1998). Compared to traditional methods for quantification of vegetation stress (Levitt, 1980), HRS is quick, exact, nondestructive and has the potential to monitor vegetation stress over broad extents (George, 1998; Yang and Chen, 2007). A wide range of hyperspectral techniques derived from the vegetation spectrum has been developed to detect anomalous gas concentrations in soil. Imaging spectrometry has been used by De Jong (1998) to detect CO_2 seepage indirectly using vegetation spectral reflectance to map the spatial and temporal extent of dead and stressed trees in the Long Valley caldera, California. Bateson et al. (2008) detected some of the gas release points via airborne remote sensing techniques at a geothermal field in central Italy where deep, naturally produced CO_2 is migrating to the surface along faults. Although the overall success rate was low, a normalized difference vegetation index (NDVI) survey was able to achieve a 47% success rate in detecting gas releasing vents. Noomen and Skidmore (2009) used the distance between red-edge position (REP) and yellow edge position (YEP) to detect CO_2 seepage using leaf reflectance.

Photosynthetic pigments such as chlorophyll *a* and chlorophyll *b* (which absorb photons that energize the reactions of photosynthesis) and carotenoids (which protect the photosynthetic reaction centers from excess light) dictate the photosynthetic potential of a leaf and relate strongly to the physiological status of plants (Blackburn, 1998). The chlorophylls (chl *a* and chl *b*) are essential pigments for the conversion of light energy to stored chemical energy (Gitelson et al., 2003). It is widely known that leaf chlorophyll content is an important parameter for testing plant health status (Kochubey and Kazantsev, 2007) and that chlorophyll content is sensitive to various types of stresses (Milton and Monat, 1989; Riggs and Running, 1991; Carter et al., 1996; Lichtenthaler, 1998). In addition, chlorophyll content gives an indirect estimation of the nutrient status because much of leaf nitrogen is incorporated in chlorophyll (Filella et al., 1995; Moran et al., 2000). Chlorophyll content tends to decline more rapidly than carotenoid content when plants are under stress (Gitelson and Merzlyak, 1994). Since increasing soil CO_2 concentrations are associated with decreasing photosynthetic pigment contents, including chlorophyll content (Vodnik et al., 2006; Noomen and Skidmore, 2009) and photosynthetic pigments control the visible spectral properties of leaves, it could be possible to detect the variations in chlorophylls and carotenoids caused by elevated soil CO_2 concentrations by calculating related spectral vegetation indices.

The derivative of reflectance can be calculated by dividing the difference between successive spectral values by the wavelength interval separating them. It can be used to locate the position of the red-edge and other peaks that may indicate stress in leaves (Smith et al., 2004b). The first derivative spectra was proposed as a means of removing sources of variability associated with broad band ratios, and to provide a more sensitive measure of stress (Horler et al., 1983). Several researchers have identified two or more peaks in first derivative spectra. Smith et al. (2004a) used ratios of the magnitude of the reflectance derivative at 725 nm to that at 702 nm to identify stress due to natural gas (methane) leakage up to 7 days before visible symptoms were observed in plants. At a site contaminated with oil, Jago and Curran (1996) identified two peaks approximately at 693 and 709 nm and found that the position of the major peak changed depending on the level of contamination within the site. Llewellyn and Curran (1999) also identified a double-peak feature in first derivative spectra and found that the shorter wavelength feature indicated high levels of soil contamination within the grassland, whereas the longer wavelength feature indicated lower levels of contamination. All these experiments used peaks in derivative spectra only in the red-edge region to detect changes in vegetation in response to CO_2 leakage and have not been used to detect stress associated with high soil CO_2 concentration. In this study, we developed a vegetation index using a negative peak (in the green spectral region) and a positive peak (in the red-edge region) in the first derivative spectra to detect vegetation stress due to high soil CO_2 concentrations.

The objective of this study was to use ground based remote sensing techniques to investigate the spectral responses of vegetation to high soil CO_2 concentrations at the Zero Emission Research and Technology (ZERT) site in Bozeman, Montana-USA, where CO_2 was injected into the shallow subsurface through a horizontal well at a depth of about 2 m. The main objectives were: (1) to assess the changes in plant chlorophyll content due to the leakage of CO_2 into the plant-soil environment, and (2) to develop an effective vegetation index derived from the first derivative reflectance values for use in detecting plant stress due to elevated concentrations of soil CO_2. The effectiveness of the vegetation index was assessed by the correlation with accumulated soil CO_2 concentration.

2. Methods

2.1. ZERT site and field experiment

A field facility has been developed by the Zero Emission Research and Technology (ZERT) in an agricultural plot at the edge of the Montana State University (MSU)-Bozeman campus in Bozeman, Montana (Spangler et al., 2009). This facility was developed to allow controlled studies of near surface CO_2 transport and detection technologies. The field has thick sandy gravel and cobble deposits overlain by a topsoil mixture of silts and clays varying in thickness from 0.2 to 1.2 m. A 100 m long horizontal well was installed at the site for the controlled release of CO_2 at a depth of approximately 2 m. On the field, the horizontal well runs southwest to northeast approximately 45^0 off true north (Fig. 1).

In the summer of 2009, a shallow CO_2 release experiment at the rate of 0.2 t/day was conducted from 12:00 pm on July 15th to 12:00 pm on August 12th. An area of $20 \times 20\ m^2$ was cordoned off for plant study. Spectral measurements were carried out along a transect perpendicular to the CO_2 injection well to study the responses of vegetation to the seepage of injected CO_2 to the ground surface. Simultaneous measurements of soil CO_2 concentration were also carried out. Vegetation species along the transect of measurement were naturally growing uncontrolled mixes dominated by Dandelion (*Taraxacum officinale*), Orchard grass (*Dactylis glomerata*) and Kentucky bluegrass (*Poa pratensis*). Plants at the ZERT site were not fertilized, irrigated, or mowed during the experiment. The Dandelions were undergoing normal mid-summer vegetative growth following flower production and the Orchard grass (*D. glomerata*) and Kentucky bluegrass (*P. pratensis*) were forming seeds after blooming. Four stations for spectral reflectance measurement were set up along the transect with station 1 situated above the CO_2 injection pipe, and station 4 approximately 7 m away from the injection pipe. Station 1 and station 2 were 1 m apart, with 3 m between remaining stations (Fig. 1). Along the same transect, four Vaisala GMT 221 CO_2 probes were deployed for soil CO_2 measurement. In order to avoid measuring spectral reflectance of possibly disturbed vegetation around the soil CO_2 probes, spectral measurement stations were not co-located with soil CO_2 probes. The soil CO_2 concentration at the spectral measurement stations was estimated by interpolating from nearby CO_2 probes using a piecewise linear method.

2.2. Spectral reflectance measurements

Spectral reflectance was measured between 336 and 1063 nm with a spectral resolution of 1 nm, covering visible and near-infrared

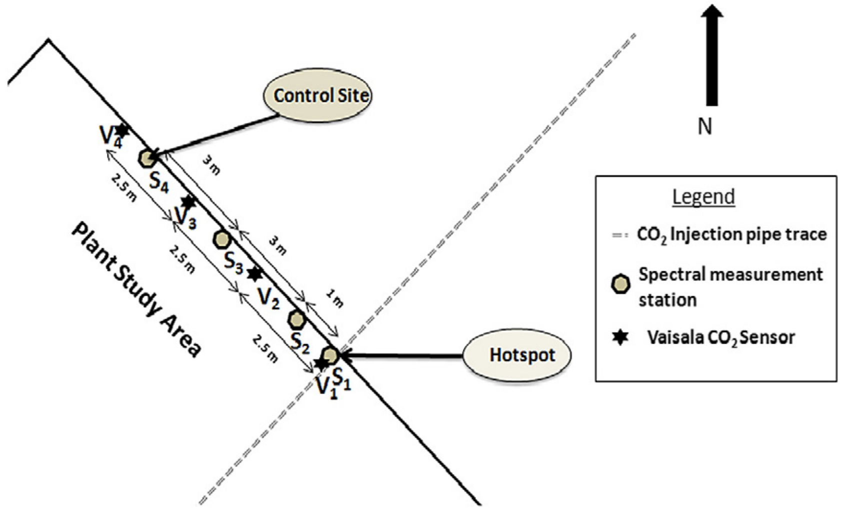

Fig. 1. Schematic diagram of the plant study area at the ZERT field facility for the summer 2009 shallow CO_2 release experiment. The transect was divided into 4 stations (S_1–S_4, shown by circles) with station 1 being on the injection pipe and station 4 approximately 7 meter away from the pipe. Stars indicate the locations of soil CO_2 concentration probes (V_1–V_4). The distance between S_1 and V_1 was 0.25 m.

portions of the electromagnetic spectrum, with an ASD Fieldspec Pro portable field spectroradiometer (ASD, Boulder, USA) fitted with a fiber optic probe having a 25° field of view. Care was taken to measure the spectral reflectance of the same spot using a tiny flag at each station as the "permanent" marker to ensured that the spectral measurements were done at exactly the same spot every time. Scans were taken from a height of 60 cm looking towards the nadir position so that the field of view at the ground was approximately 27 cm in diameter, hopefully big enough to minimize impact due to any possible small displacements of the footprint of the sensor at different times. Measurements were taken within 2 h around solar noon under clear sky conditions. All scans were optimized and referenced against a white reference panel before scanning the vegetation at all four stations. About 30 scans per measurement were taken at each station to increase the signal/noise (S/N) ratio. A total of eight spectral measurements were made at each station during the CO_2 release. During the one month that CO_2 was released, 8 days had clear sky conditions suitable for field measurements with the ASD spectroradiometer.

2.3. Soil CO_2 concentration measurements

Soil CO_2 concentration was measured by the Montana State University (MSU) research group using Vaisala GMT 221 CO_2 probes with in-soil adapters buried at a depth of approximately 30 cm over the injection pipe and at 2.5, 5, and 7.5 m away from the injection pipe (Fig. 1). These probes can measure CO_2 in the range of 0–20% volume. At station 1, approximately 1.5 h after the injection started, the soil CO_2 concentration increased quickly above the calibration range of the soil CO_2 probe. Because of this, spectral reflectance data at station 1 were excluded from the regression analyses with the accumulated soil CO_2 concentration in the following discussion.

2.4. Spectral data analysis

Field spectral reflectance was measured using the field spectroradiometer with a calibrated white reference panel. In order to estimate the change in chlorophyll content of the leaves due to leakage of CO_2, reflectance band ratios related to chlorophyll content were calculated. Variations in background reflectance properties, contributions from non-photosynthetic canopy components and the effects of leaf layering and canopy structure may weaken the relations between reflectance values in single wavebands and pigment concentrations. Pigment indices which use ratios of reflectance at different wavelengths may overcome such difficulties (Blackburn, 1998). In this study, structural independent pigment index (SIPI) (Eq. (1)) (Penuelas et al., 1995), chlorophyll normalized difference index (Chl NDI) (Eq. (2)) (Richardson et al., 2002), pigment specific simple ratios for chlorophyll *a* (PSSR*a*) (Eq. (3)) and chlorophyll *b* (PSSR*b*) (Eq. (4)) (Blackburn, 1998) were used to estimate the change in chlorophyll content of the plants and these indices were correlated with the accumulated soil CO_2 concentrations to study the accumulated impact due to CO_2 leakage on chlorophyll content of the plants. In the visible spectral region, the high absorption of radiation energy is due to leaf pigments; primarily the chlorophylls and carotenoids (Knipling, 1970) and therefore it would be possible to track changes in chlorophyll content by calculating vegetation indices in the visible spectrum. Since SIPI compares carotenoids with chlorophyll *a*, Chl NDI is an indicator of total chlorophyll content and PSSR*a* and PSSR*b* are the indicators of chlorophyll *a* and chlorophyll *b*, these indices were chosen to estimate changes in the concentrations of carotenoids, total chlorophyll, chlorophyll *a* and chlorophyll *b*.

$$\mathrm{SIPI} = (R_{800} - R_{445}) / (R_{800} - R_{680}) \tag{1}$$

where R_{445}, R_{680} and R_{800} are the spectral reflectance values at 445, 680 and 800 nm, respectively.

$$\mathrm{Chl\ NDI} = (R_{750} - R_{705}) / (R_{750} + R_{705}) \tag{2}$$

where R_{705} and R_{750} are the spectral reflectance values at 705 and 750 nm, respectively.

$$\mathrm{PSSR}a = R_{800} / R_{675} \tag{3}$$

$$\mathrm{PSSR}b = R_{800} / R_{650} \tag{4}$$

where R_{650}, R_{675} and R_{800} are the spectral reflectance values at 650, 675 and 800 nm, respectively.

Derivative spectra were calculated by differentiating the spectral reflectance with respect to wavelength. The wavelengths at which the first derivative spectra reach maximum and minimum values were used to derive a vegetation index to quantify the difference between CO_2 stressed and control vegetation. In the first derivative spectra, for CO_2-stressed vegetation at stations 2 and 3, the minimum (negative) was found to locate between 575 nm and 580 nm and the maximum (positive) was between 720 nm and 723 nm. The wavelengths at these two features (minimum and maximum) were selected manually and used to derive the Normalized difference First Derivative Index (NFDI). The averages of the first derivative values of spectral reflectance between 575 nm and 580 nm were calculated and their absolute values were then taken. The averages of the first derivative values of spectral reflectance between 720 nm and 723 nm were also calculated. NFDI was calculated as follows based on these average values:

$$\mathrm{NFDI} = (\mathrm{d}R_{720-723} - \mathrm{d}R_{575-580}) / (\mathrm{d}R_{720-723} + \mathrm{d}R_{575-580}) \quad (5)$$

where $\mathrm{d}R_{575-580}$ is the average of the absolute first derivative values between 575 nm and 580 nm, and $\mathrm{d}R_{720-723}$ is the averaged first derivative values between 720 nm and 723 nm. The *T*-test was performed on the statistical results to determine whether differences in NFDI values were significant between stressed and control vegetation.

The CO_2 release was at a constant rate and there was little variation in the soil CO_2 concentration at these stations, while the vegetation deteriorated with time during the time period of CO_2 release. The overall accumulated soil CO_2 concentration was calculated by integrating the time series of measured CO_2 concentration (% in volume) over time (day) from the point when the CO_2 release started at 12:00 pm July 15, 2009. The unit for the accumulated soil concentration is thus %day, indicating a day's accumulated exposure of the plants to the soil CO_2 concentration. One %day is equivalent to an exposure of vegetation to 1% soil CO_2 concentration above the background CO_2 level for a whole day (24 h). The background CO_2 does not negatively impact vegetation, but is an indicator of the respiration activity of vegetation and soil. We assumed the background soil CO_2 concentration is constant before and during the CO_2 release and the accumulated background CO_2 is subtracted from the overall accumulated CO_2 using the average background CO_2 measured before the commencement of the CO_2 release. The result is called background-corrected accumulated CO_2. We will call it simply accumulated CO_2 concentration in the following discussion. The time series of accumulated soil CO_2 concentrations at stations 2, 3 and 4 are shown in Fig. 2. Analysis of the spectral reflectance with the instantaneous value of soil CO_2 concentration showed a weak correlation between them (data not shown here). On the other hand, any biological response to a stimulus or stressing factor needs time, some short and others long. Therefore we hypothesized that the vegetation spectral reflectance was sensitive to the accumulated soil CO_2 concentration. For each of the correlation analyses below, Pearson's correlation coefficient was calculated to investigate how the vegetation indices are impacted by the accumulated CO_2 and linear regression was used to plot the line of best fit.

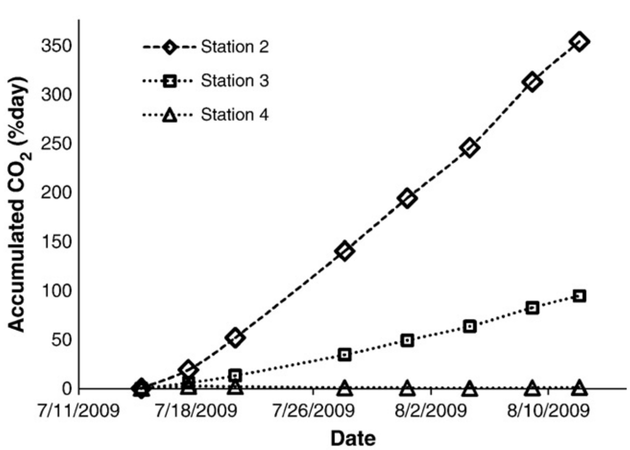

Fig. 2. Accumulated soil CO_2 concentration (%day) during the CO_2 injection experiment. Instantaneous soil CO_2 concentraton ranged 0.6–19% for station 2 and 1–6.5% for staton 3. For station 4, soil CO_2 concentration was almost stable (1.5–1.0%), indicating background normal soil CO_2 levels.

3. Results

3.1. Soil CO_2 concentrations

At station 4, soil CO_2 concentrations ranged between 1.5 and 1.0% during the CO_2 injection period. Normal soil air contains around 0.5–2% CO_2 (Russel, 1973), so station 4 was considered as a control site. At station 2, which was at 1 m distance from the injection well, the soil CO_2 concentration ranged between 0.6 and 19% by volume. The maximum concentration measured at this station was approximately 13 times greater than background soil CO_2 concentration (1.5%). At station 3, the soil CO_2 concentrations were intermediate and rose to approximately 6.5% CO_2 by volume.

3.2. Visible stress symptoms

Dandelion (*T. officinale*) plants at station 1 (Fig. 1) showed visible stress symptoms in the form of purple discoloration of leaves within a week after the beginning of the CO_2 injection (Fig. 3). The visible impact area extended approximately 0.5 to 1 m radially from station 1, where the high soil CO_2 concentrations (>20%) were measured. Dandelion (*T. officinale*) leaves were completely dead at station 1 after two weeks from the beginning of the CO_2 release. At station 2, where lower soil CO_2 concentration was observed, visible stress expression of plant leaves was not evident until two weeks into the experiment. Then the edges of the Dandelion (*T. officinale*) leaves became purple, but with a smaller degree of discoloration in comparison to station 1, but eventually the leaves died by the end of the experiment. Little visible stress (purple discoloration) was evident at station 3 and this discoloration was not observed at the control site.

Compared with Dandelion (*T. officinale*), both Orchard grass (*D. glomerata*) and Kentucky bluegrass (*P. pratensis*) appeared to be more resistant to CO_2 leakage and did not show any visible stress symptoms, such as yellowing, until two weeks into CO_2 injection, when they became increasingly chlorotic at station 1. Chlorotic leaves produce insufficient chlorophyll and therefore appear yellow (Adams et al., 1999). At station 2, both the grass species showed visible stress by becoming yellow by the end of the third week of the experiment. No such chlorosis was found at the remaining stations for both grass species. Overall, different plant species showed different degrees of visible stress symptoms. Dandelion (*T. officinale*) plants appeared to be more sensitive to higher levels of CO_2 in the soil than Orchard grass (*D. glomerata*) or Kentucky bluegrass (*P. pratensis*). All three species showed a decreasing gradient in visible stress from station 1 to station 4, in response to a similar gradient in-soil CO_2 concentration from station 1 to station 4.

3.3. Chlorophyll content status estimation using vegetation indices

Pigment concentration dictates the photosynthetic potential of leaves and relates strongly to their physiological status (Blackburn, 1998). Decrease in chlorophyll content of the leaves is often used as an indicator of plant stress because it is a typical response regardless of species or cause of stress (Carter, 1993). Since photosynthetic pigments control the spectral reflectance properties of leaves, especially in the visible spectral region, we attempted to assess chlorophyll and carotenoid content by using relevant vegetation indices.

3.3.1. Structural independent pigment index (SIPI)

Structural independent pigment index (SIPI) has been used by Penuelas et al. (1995) to accurately estimate the ratio of carotenoids to chlorophyll *a*. It employs spectral reflectance ratio values at 445 nm, 680 nm and 800 nm, where 445 nm and 680 nm correspond to the *in vivo* absorption maxima of carotenoids and chlorophyll *a* respectively, and the 800 nm band is incorporated to minimize the confounding effects of leaf structure. Fig. 4 shows the correlation

Fig. 3. Photographs showing vegetation on 14th of July 2009 and 28th of July 2009. Photographs in the left column show the healthy vegetation before starting the CO_2 injection. Photographs in the right column show the decreasing degree of visible stress from station 1 to station 4 after two weeks of the beginning of CO_2 injection.

between SIPI and the accumulated soil CO_2 concentration data for station 2 and station 3, where stressed vegetation was observed, and station 4, where vegetation did not show signs of stress. SIPI was positively correlated ($r = 0.90$; $p = 0.002$) with the accumulated soil CO_2 concentration at station 2, indicating an increase in the carotenoids/chlorophyll *a* ratio. The same positive correlation was found at station 3 with the correlation coefficient $r = 0.80$ ($p = 0.017$). Since there is a complementary relation between carotenoids and chlorophylls, this result suggests that there was a decrease in chlorophyll *a* concentration or an increase in carotenoid concentration. At station 4, there was a negative linear relation ($r = -0.35$; $p = 0.395$). The correlation was not significant at the 95% level, but the reverse of sign in the correlation coefficient from positive at stations 2 and 3 to negative at station 4 indicates that there was an increase in chlorophyll *a* concentration at the control site. As the CO_2 concentration at station 4 during the CO_2 release and after release was almost the same, this increase indicates the natural growth of the vegetation at the site.

3.3.2. Chlorophyll normalized difference index (Chl NDI)

Normalized difference vegetation index (NDVI) is generally derived from broad red and near-infrared wavebands and can be used to measure the fraction of absorbed photosynthetically active radiation and green vegetation cover at the canopy to global scales (Kumar and Monteith, 1981; Gamon et al., 1995). Gitelson and Merzlyak (1994) suggested that using a narrow waveband at the edge of the chlorophyll absorption feature (i.e., at 705 nm) rather than in the middle could yield a better linear correlation between NDVI and chlorophyll content. Fig. 5 shows the scatter plots relating Chl NDI to the accumulated soil CO_2 concentration at stations 2, 3 and 4. The

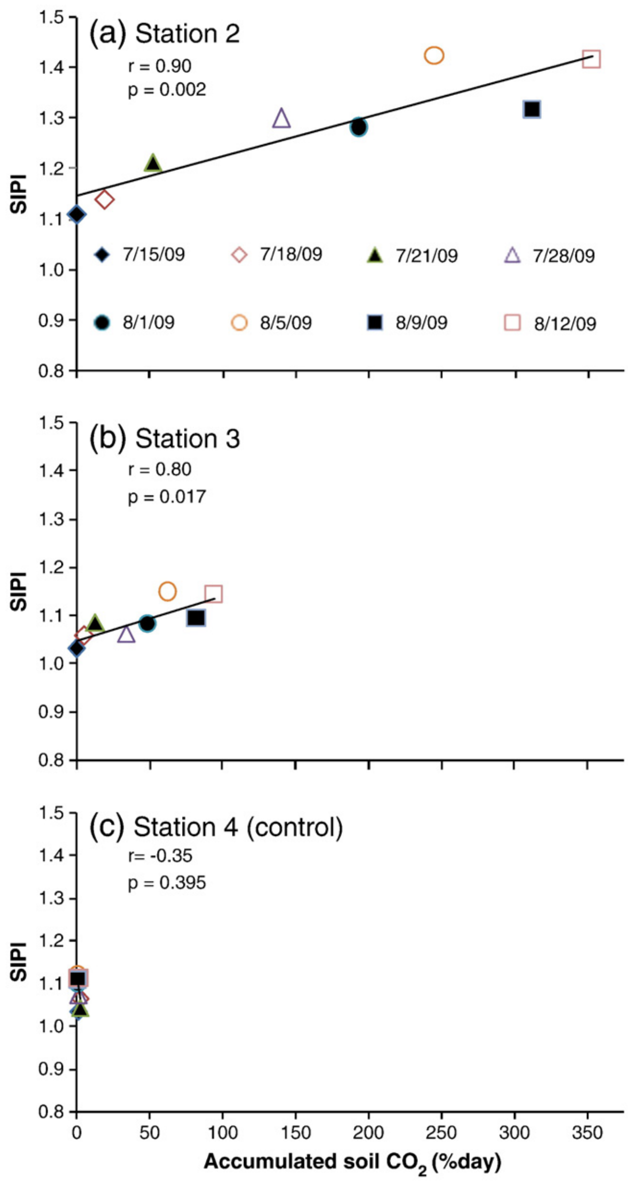

Fig. 4. Correlation between structural independent pigment index (SIPI) and accumulated soil CO_2 percent data for: (a) station 2 and (b) station 3, positive correlations ($r = 0.90$ and $r = 0.80$) indicates an increase in carotenoids/chlorophyll *a* concentration, (c) Station 4, correlation ($p = 0.395$) is not significant at 95% level, indicating no effect of leaking CO_2. Dates of data collection and corresponding symbols are indicated in (a).

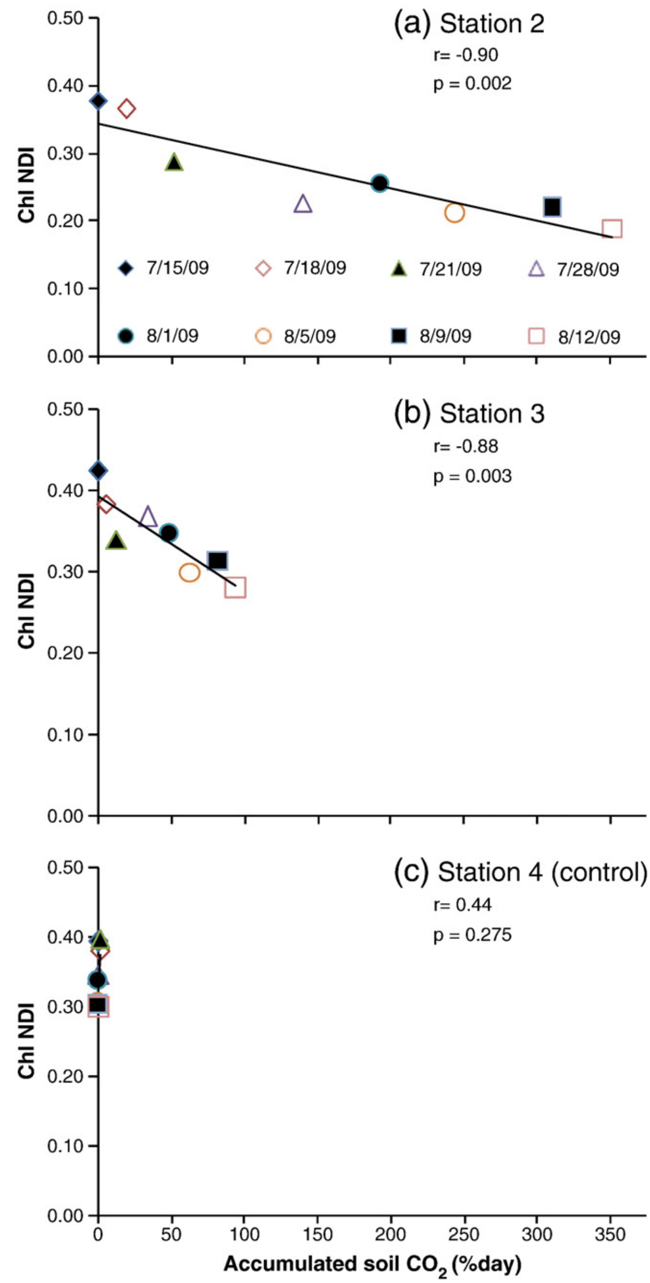

Fig. 5. Scatter plots indicating the relationship between chlorophyll normalized difference vegetation index (Chl NDI) and accumulated soil CO_2 for (a) stations 2, (b) station 3, and (c) station 4. The negative correlation at stations 2 and 3 was due to a decrease in chlorophyll content of leaves and the positive correlation at station 4 indicates no effect of CO_2 leakage. Dates of data collection and corresponding symbols are indicated in (a).

relationship was linear and negative for stations 2 and 3 and had high correlation coefficient values ($r = -0.90$; $p = 0.002$ and $r = -0.88$; $p = 0.003$ respectively at station 2 and station 3), indicating there was a decrease in chlorophyll content associated with high soil CO_2 concentration. For station 4, there was a positive linear relationship ($r = 0.44$; $p = 0.275$). Similar to the SIPI index, the correlation was not significant at the 95% level but the reverse of sign in the correlation coefficient from negative (stations 2 and 3) to positive (station 4) also indicates the natural growth of vegetation in this season.

3.3.3. Pigment specific simple ratios (PSSRa and PSSRb)

Both pigment specific simple ratios (PSSR*a* and PSSR*b*) use the 800 nm waveband to minimize the effects of radiation interactions at the leaf surface and internal structures in the mesophyll (Penuelas et al., 1995). The basis for choosing the 650 nm and 675 nm wavebands is that they represent absorption maxima of chlorophyll *a* and chlorophyll *b* respectively (Chappelle et al., 1992). Fig. 6 shows that both PSSR*a* and PSSR*b* exhibit a similar pattern to SIPI and Chl NDI at stations 2 and 3. Both indices have strong correlations ($r = -0.86$; $p = 0.006$ and $r = -0.86$; $p = 0.006$) with the accumulated soil CO_2 concentration at station 2 and showed negative linear trends. The same negative linear trend was observed at station 3 and the correlation coefficient values for PSSR*a* and PSSR*b* were -0.77 ($p = 0.024$) and -0.73 ($p = 0.037$), respectively. A positive linear trend between indices and the accumulated soil CO_2 concentration ($r = 0.26$ and $r = 0.28$ respectively for PSSR*a* and PSSR*b*) was observed at station 4. The correlations were not significant at the 95% confidence level, but the reverse of sign in the correlation coefficient also indicates the increase of chlorophyll *a* and *b* at the control site due to the natural growth in this season, similar to the SIPI and Chl NDI indices (Fig. 9).

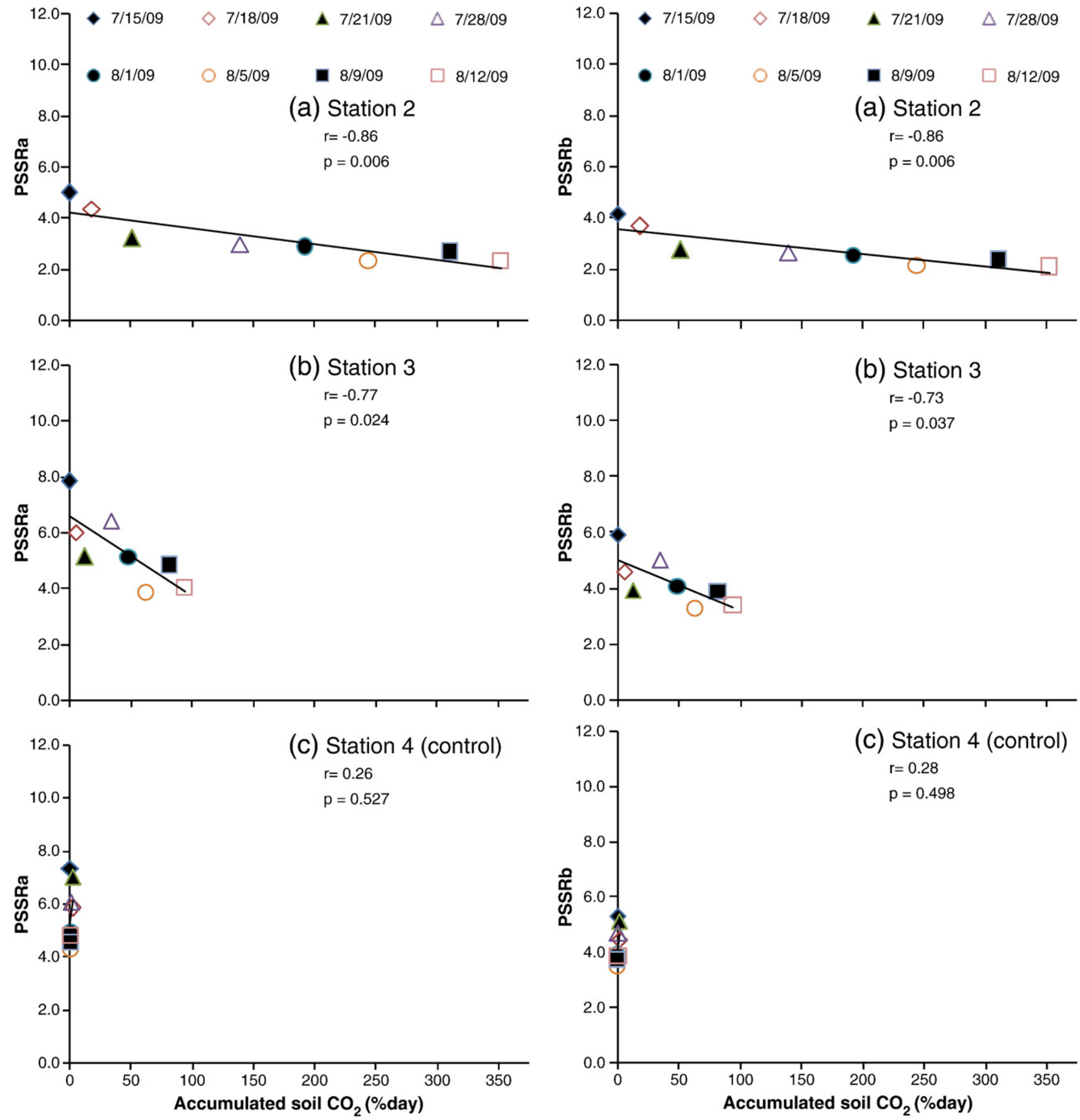

Fig. 6. Both PSSR*a* and PSSR*b* have negative linear trends at stations 2 and3, indicating a decrease in chlorophyll *a* and chlorophyll *b* concentration with increasing levels of soil CO_2. At station 4, the correlation shows a poor relationship with soil CO_2 and thereby indicates natural growth of vegetation at this site was unaffected by the leaking CO_2. Dates of data collection and corresponding symbols are indicated in (a).

3.4. Normalized difference first derivative index (NFDI)

A typical first derivative curve of spectral reflectance with respect to wavelength at station 2 is shown in Fig. 7 for July 18, 2009. The first derivative curves for other days are similar in pattern but different in magnitude. Fig. 8 shows the relationship between the NFDI and the accumulated soil CO_2 concentration at stations 2, 3 and 4. At stations 2 and 3, the correlation is negative, indicating a linear decrease in the index as the amount of accumulation of CO_2 increases. At station 4, the correlation is positive, indicating natural growth at the control site. NFDI was more strongly correlated with the accumulated soil CO_2 ($r = -0.93$; $p = 0.0008$). The change in the value of NFDI at station 2 between first day ($t = 1$ d; 15th July 2009) and last day ($t = 29$ d; 12th August 2009) of the CO_2 injection was 36% and for the control station (station 4), the change was 1% only. The correlation coefficient was $r = -0.71 (p = 0.048)$ at station 3. At station 4, the correlation between NFDI and the accumulated soil CO_2 ($r = 0.33$, $p = 0.424$) is not significant at the 95% level. This indicates that NFDI is not sensitive to normal growth of vegetation. Since the soil CO_2 concentration at station 4 is almost equal to the background CO_2 concentration due to soil and root respiration, the significance of the correlation is not expected to be high.

4. Discussion

At station 1 (situated over the injection well), soil CO_2 concentration was above the calibration range of the sensor indicating elevated levels of CO_2 in the soil air. At station 2 (1 m away from the injection

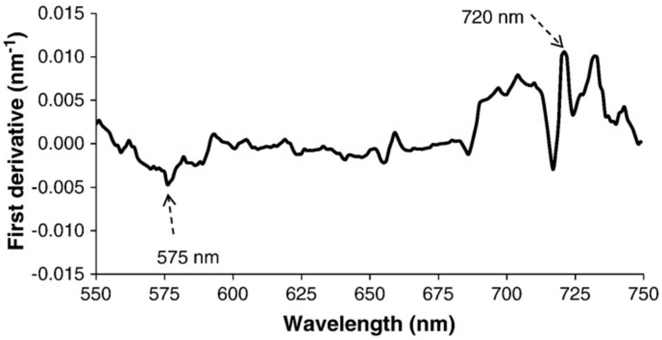

Fig. 7. The typical first derivative of reflectance with respect to wavelength of mixed vegetation on 7/18/2009 at station 2 of the transect. The arrows indicate the positions of local extremes used to generate normalized difference first derivative index (NFDI).

well), soil CO_2 rose to a maximum of 19% by volume. At station 3 which was at a distance of 4 m from the injection well, a maximum of 6.5% soil CO_2 by volume was measured. Compared to stations 1–3, the soil CO_2 concentration at station 4 was low enough to be considered a control site. A very sharp gradient of soil CO_2 exists. This sharp gradient indicates limited lateral diffusion of CO_2 leaking from the injection well resulting from low gaseous conductance of the silty-clay soil typical of the site. Vodnik et al. (2006) reported limited lateral diffusion of soil CO_2 at a natural CO_2 spring (mofette) field in NE Slovenia caused by low conductance of CO_2 in silty-clay soil and concluded that vertical flux was a dominant part of CO_2 movement. Noomen et al. (2008) also found the extent of high gas/low oxygen area due to low porosity of a clay layer was small in a simulated natural gas leakage experiment.

At open sites, CO_2 concentrations in the atmosphere do not reach values as high as those measured in the soil and strongly depend on microclimatic situations such as wind speed and direction (Pfanz et al., 2004). Vodnik et al. (2006) reported a very sharp gradient in CO_2 concentration at the soil/atmosphere interface and measured soil CO_2 concentration up to 100% at a depth of 20 cm, while the atmospheric CO_2 concentration at the soil surface and at a height of 10 cm reached the range of a few percent or stayed below 0.5%, respectively. Since the experiment was conducted in an open agricultural plot, it was believed that the main impact of CO_2 leaking from the injection pipe on vegetation was at the root zone. If the CO_2 leak is sufficient enough to alter ambient atmospheric levels, it can impact plant habitus, as well as organ morphology, tissue anatomy, physiology and biochemistry (Pfanz et al., 2004). However, the level of enrichment in the atmosphere depends on the volume of CO_2 released, the distance from the leak, and on horizontal and vertical transport processes (Miglietta et al., 1993).

Vegetation at stations 2 and 3 showed visible stress symptoms as well as spectral reflectance changes. Purple discoloration of Dandelion (*T. officinale*) leaves was evident above the area of highest soil CO_2 concentration. This purple discoloration was evident within a week after beginning the CO_2 injection. Smith et al. (2005) reported that the injection of natural gas into soil caused oilseed rape leaves to turn purple eight days after gas flow commenced. High soil CO_2 concentrations are associated with low O_2 concentrations (Hoeks, 1972b) and thus inhibit the root respiration that provides energy for root growth and uptake of nutrients from soil (Hoeks, 1972a; Gilman et al., 1982; Arthur et al., 1985). Phosphorus stress could increase anthocyanin production and thereby cause purple discoloration of leaves (Marschner, 1995). Anthocyanins are light-intercepting pigments in the vacuoles of cells in the upper leaf blade layers and are regarded as defense compounds (Dixon and Paiva, 1995). However, it has to be verified that this effect was due to nutrient stress caused by CO_2.

Elevated soil CO_2 concentration caused chlorosis in grass after two weeks into CO_2 injection. This yellow color of leaves indicates the reduction of chlorophyll and is one of the most obvious visual

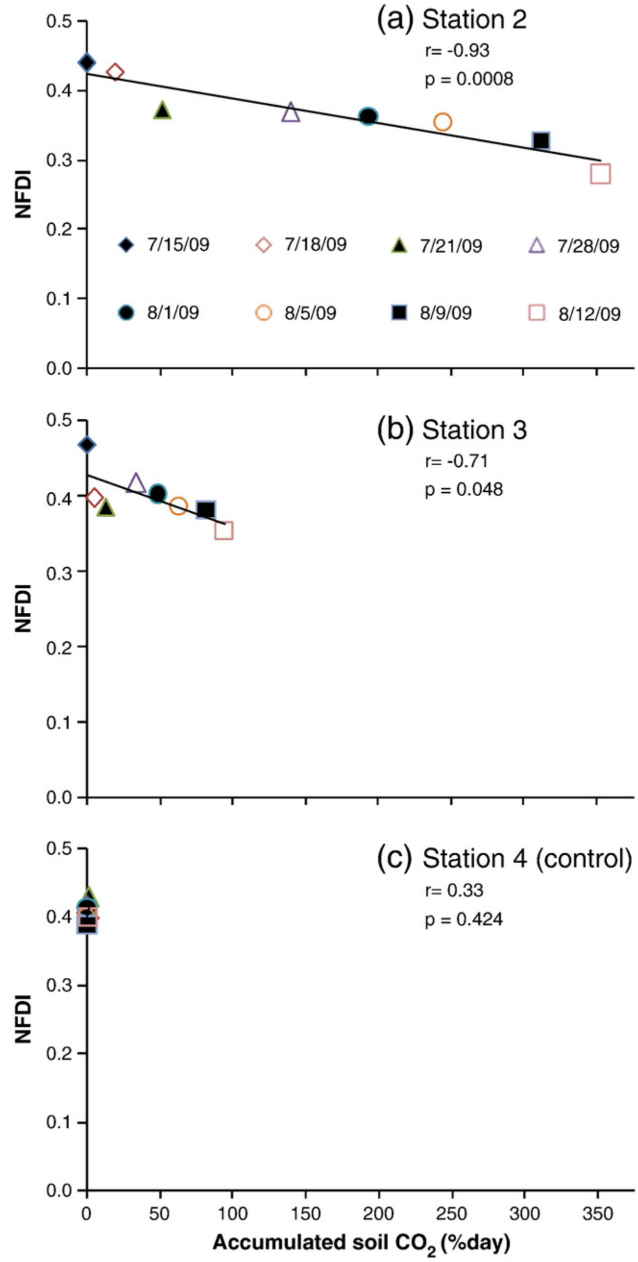

Fig. 8. Normalized difference first derivative index (NFDI) plotted against accumulated soil CO_2 percent at (a) station 2, (b) station 3, and (c) station 4 along the transect of measurement. High correlations at stations 2 and 3 between NFDI and soil CO_2 enable us to use NFDI as a potential hyperspectral index to identify higher levels of soil CO_2 concentration. A weak correlation at station 4 was an expected result because of background levels of soil CO_2 at this station. Dates of data collection and corresponding symbols are indicated in (a).

indications of plant stress (Adams et al., 1999). Chlorosis can be easily recognized and serve as a semi-quantitative visual index of the severity of nutritional and other disorders (Weiss, 1943). Smith et al. (2004a) found a circle of chlorosis approximately 50 cm in diameter and reduction in growth of the grass around the area of natural gas injection. These symptoms of stress were visible after 44 days in an early-stage (germinating seeds) gassing experiment and after 32 days in a late-stage (fully established crop) gassing experiment. In another study, Smith et al. (2004b) found that soil oxygen depletion caused stress effects in pot-grown barley and beans between 14 and 21 days after starting treatment. Pysek and Pysek (1989) reported that symptoms were visible in various species of vegetation between 15 and 30 days after exposure to a leaking natural gas main.

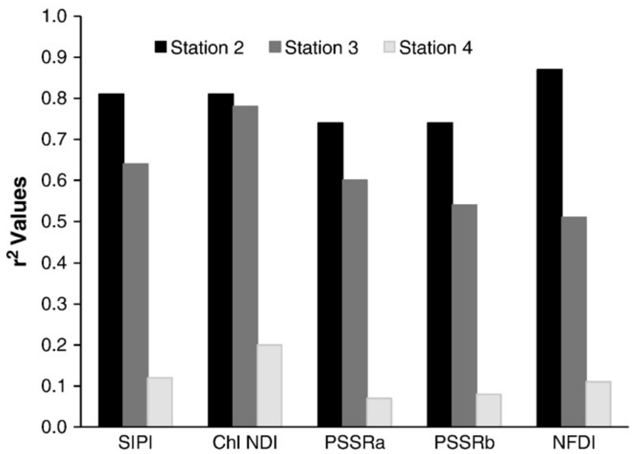

Fig. 9. Summary of results, illustrating coefficient of determination (r^2) values for the indices used to assess the chlorophyll/carotenoid content status of plants and to detect plant stress (NFDI) at stations 2, 3 and 4 along the transect of measurement. High correlation values at station 2 indicate the change in pigment concentration due to elevated soil CO_2 concentration.

Generally a plant leaf has low reflectance in the visible spectral region because of strong absorption by chlorophylls and a relatively high reflectance in the near-infrared region because of strong internal scattering within the leaf (Knipling, 1970). At the stations with elevated soil CO_2, the vegetation showed an increase in visible reflectance and a decrease in near-infrared reflectance when compared with the control vegetation. This increase in visible reflectance may be an indicator of stress resulting from oxygen displacement by increasing soil CO_2. Several researchers reported a similar increase in visible reflectance in response to stress due to soil oxygen depletion. In an experiment to determine the effects of soil oxygen displacement on pot-grown plants, Smith et al. (2004b) found an increased visible reflectance with little difference in near-infrared region irrespective of the oxygen displacement method used. Pysek and Pysek (1989) found that natural gas leakage increased reflectance at red wavelengths and decreased near-infrared reflectance. Carter (1993) found consistently increased visible reflectance in response to stress in various plant species with different stress agents. During the ZERT experiment, plants exposed to soil CO_2 concentration levels greater than 6.5% showed significant changes in their spectral responses as compared to plants at the control site. This is consistent with the observation by Bateson et al. (2008) that the minimum soil CO_2 concentration that can be detected at gas vents was 5.6%.

The processes that govern the behavior of the spectral reflectance in the near-infrared range and visible spectrum are very different. An increase in leaf thickness and/or density may increase reflectance in the near infrared region and an increase in the visible reflectance indicates a decrease in pigment content (Gitelson et al., 2003). All four indices used to assess changes in chlorophyll concentration show a decrease in chlorophyll content for vegetation at stations of elevated soil CO_2 when compared to control vegetation. SIPI showed a positive correlation with increasing soil CO_2, indicating an increase in the carotenoids/chlorophyll *a* ratio. This is likely because of chlorophyll degradation. Higher values of SIPI at station 2 compared to the control site also suggest a higher carotenoids to chlorophyll ratio. Increases in relative concentration of carotenoids are often observed when plants are subjected to stress (Margalef, 1974; Young and Britton, 1990). Penuelas et al. (1994) showed that the ratio of carotenoids to chlorophyll *a* increased in senescing and unhealthy plants and decreased in healthy plants. Chl NDI was substantially better correlated with increasing accumulated soil CO_2 concentrations, showing a decrease in the index value as indicated by the negative linear trend in Fig. 5(a). Since Chl NDI is an indicator of the chlorophyll content of leaves, this result shows that plants exposed to higher soil CO_2 levels have suffered a decrease in chlorophyll content. Sims and Gamon (2002) examined hundreds of leaves of non-related plant species and proved that Chl NDI was the most sensitive indicator of chlorophyll content. The correlation between either PSSR*a* or PSSR*b* with soil CO_2 concentration also supports the observation that chlorophyll content decreased with accumulated soil CO_2 exposure. All these results suggest that there was a decrease in chlorophyll content of the plants with increasing levels of soil CO_2. This is consistent with Noomen and Skidmore's (2009) observation that increasing CO_2 concentrations reduce leaf chlorophyll content. Huang et al. (1997) demonstrated that 10% CO_2 in combination with 5% O_2 in the soil significantly decreased photosynthesis and leaf chlorophyll of wheat cultivars. The present study is in agreement with the previous results that increasing soil CO_2 is tied to a decrease of leaf chlorophyll. As expected, all four indices (SIPI, Chl NDI, PSSR*a* and PSSRb) yield very poor correlation with accumulated soil CO_2 concentration at the control site (station 4). However, though the correlation at the control site is weak, the reverse correlation compared with stations 2 and 3 remains evident, and indicates the natural growth of vegetation at the control site.

First derivatives of reflectance provide a sensitive analysis of the subtle spectral absorption and reflectance features associated with vegetation stress (Philpot, 1991; Dawson and Curran, 1998). At the spectral sampling interval typical of hyperspectral systems, derivatives should also be relatively less sensitive to the spectral variations of sunlight and skylight (Tsai and Philpot, 1998). A very clear feature in the first derivative spectra was the double-peak in the red-edge region. A single peak was observed between 720 nm and 723 nm that did not shift, but the magnitude of the peak decreased as vegetation became stressed. Similarly, the second peak, positioned between 730 nm and 733 nm, did not shift and decreased in magnitude with increasing stress. Here first derivative spectra were used to derive the NFDI vegetation index that can be used to identify plant stress associated with elevated levels of subsurface soil CO_2.

At station 2, NFDI negative correlation with the accumulated soil CO_2 concentration, indicates a linear decrease in the index values with increasing levels of soil CO_2. The Student's *T*-test revealed that NFDI values were statistically significantly ($p = 0.01$) different between stressed and control plants at 99% confidence level. The percent change in index value at station 2 during the CO_2 injection experiment was 36%. At the control station (station 4), soil CO_2 concentration was almost stable during the experiment and was within the range of 1.5–1.0%, indicating background soil CO_2 levels. The percent change in NFDI at this station during the experiment was 1% and thus resulted in a very weak correlation between NFDI and accumulated soil CO_2 at this station. Strong correlations at stations 2 and 3 indicate that NFDI developed in this study was able to identify plant stress responses associated with elevated soil CO_2 concentrations. Comparing the stressed vegetation station (station 2) to the control site, there was a continuous decrease in the magnitude of both maximum and minimum peak values of derivative spectra from the first day (July 15th, 2009) to the last day (August 12th, 2009) of CO_2 release. Since NFDI is derived based on these changes and we hypothesized that these changes are stress induced responses of plants due to soil oxygen depletion caused by elevated CO_2, NFDI could be a potential indicator to detect stress effects in vegetation due to increased levels of CO_2 in the soil. However, as other stress agents could also deplete soil oxygen or cause similar changes in the derivative spectra, future research is necessary to evaluate the potential use of NFDI to detect plant stress associated with higher soil CO_2 levels.

5. Conclusions

Hyperspectral remote sensing was used to investigate the responses of plants to simulated leakage of sequestered CO_2. Elevated CO_2 concentrations in plant-soil environment resulting from the leakage caused stress in vegetation which was detectable by visible symptoms (purple discoloration and chlorosis) and changes in spectral reflectance. Changes in spectral pattern were evident with an increase in spectral reflectance in the visible region and a decrease in spectral reflectance in the near-infrared region. The increase in spectral reflectance in the visible region may be a generic response of plants to stress induced changes in chlorophyll concentration. The vegetation indices tested in this study to assess chlorophyll content showed that increasing levels of accumulated soil CO_2 concentration decreased chlorophylls (chlorophyll *a* and chlorophyll *b*) and increased carotenoid concentration. First derivative reflectance spectra were used to detect leakage of CO_2 into plant-soil environment. There was a continuous decrease in the first derivative features at 575–580 nm and 720–723 nm with increasing accumulated soil CO_2 levels, and these two features were used to develop a vegetation index (NFDI) that could be used to detect stress due to elevated soil CO_2 concentration. NFDI had a significant correlation ($p<0.01$) with higher levels of accumulated soil CO_2 concentration, showing the elevated differences in magnitude between stressed and control plants and thus could be used in detecting stress gradients in vegetation induced by elevated levels of soil CO_2. These results suggest that stress and stress induced responses such as a decrease in chlorophyll concentration due to elevated soil CO_2 could be detected by measuring changes in spectral reflectance of overlying vegetation and thereby showing the potential application of hyperspectral remote sensing to monitor geologic CO_2 sequestration sites.

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References

Adams, M.L., Philpot, W.D., Norvell, W.A., 1999. Yellowness index: an application of spectral second derivatives to estimate chlorosis of leaves in stressed vegetation. International Journal of Remote Sensing 20 (18), 3663–3675.

Arthur, J., Leone, I., Flower, F., 1985. The response of tomato plants to simulated landfill gas mixtures. Journal of Environmental Science and Health A20 (8), 913–925.

Bateson, L., Vellico, M., Beaubien, S.E., Pearce, J.M., Annunziatellis, A., Ciotoli, G., Coren, F., Lombardi, S., Marsh, S., 2008. The application of remote-sensing techniques to monitor CO_2 storage sites for surface leakage: method development and testing at Latera (Italy) where naturally produced CO_2 is leaking to the atmosphere. International Journal of Greenhouse Gas Control 2, 388–400.

Blackburn, G.A., 1998. Spectral indices for estimating photosynthetic pigment concentrations: a test using senescent tree leaves. International Journal of Remote Sensing 19, 657–675.

Boru, G., Vantoai, T., Alves, J., Hua, D., Knee, M., 2003. Responses of soybean to oxygen deficiency and elevated root-zone carbon dioxide concentration. Annals of Botany 91, 447–453.

Carter, G.A., 1993. Responses of leaf spectral reflectance to plant stress. American Journal of Botany 80, 239–243.

Carter, G.A., 1994. Ratios of leaf reflectances in narrow wavebands as indicators of plant stress. International Journal of Remote Sensing 15, 697–703.

Carter, G.A., 1998. Reflectance bands and indices for remote estimation of photosynthesis and stomatal conductance in pine canopies. Remote Sensing of Environment 63, 61–72.

Carter, G.A., Cibula, W.G., Miller, R.L., 1996. Narrow-band reflectance imagery compared with thermal imagery for early detection of plant stress. Journal of Plant Physiology 148, 515–520.

Chappelle, E.W., Kim, M.S., McMurtrey III, J.E., 1992. Ratio analysis of reflectance spectra (RARS): an algorithm for the remote estimation of the concentrations of chlorophyll A, chlorophyll B, and the carotenoids in soybean leaves. Remote Sensing of Environment 39, 239–247.

Dawson, T.P., Curran, P.J., 1998. A new technique for interpolating the reflectance red edge position, Technical note. International Journal of Remote Sensing 19 (11), 2133–2139.

De Jong, S., 1998. Imaging spectrometry for monitoring tree damage caused by volcanic activity in the Long Valley caldera, California. ITC journal 1, 1–10.

Dixon, R.A., Paiva, N.L., 1995. Stress-induced phenylpropanoid metabolism. The Plant Cell 7, 1085–1097.

Drew, M.C., 1991. Oxygen deficiency in the root environment and plant mineral nutrition. In: Jackson, M.B., Davis, D.D., Lambers, H.L. (Eds.), Plant Life under Oxygen Deprivation. SPB Academic Publishing, The Hague, pp. 303–316.

Filella, I., Serrano, I., Serra, J., Penuelas, J., 1995. Evaluating wheat nitrogen status with canopy reflectance indices and discriminant analysis. Crop Science 35, 1400–1405.

Gamon, J.A., Field, C.B., Goulden, M., Griffin, K., Hartley, A., Joel, G., Penuelas, J., Valentini, R., 1995. Relationships between NDVI, canopy structure, and photosynthetic activity in three Californian vegetation types. Ecological Applications 5, 28–41.

George, A.B., 1998. Quantifying chlorophylls and carotenoids at leaf and canopy scales: an evaluation of some hyperspectral approaches. Remote sensing of environment 39, 329–335.

Gilman, E., Leone, I., Flower, F., 1982. Influence of soil gas contamination on tree root health. Plant and Soil 65, 3–10.

Gitelson, A., Merzlyak, M.N., 1994. Spectral reflectance changes associated with autumn senescence of *Aesculus hippocastanum* L. and *Acer platanoides* L. leaves. Spectral features and relation to chlorophyll estimation. Journal of Plant Physiology 143, 286–292.

Gitelson, A., Gritz, Y., Merzlyak, M.N., 2003. Relationships between leaf chlorophyll content and spectral reflectance and algorithms for non-destructive chlorophyll assessment in higher plant leaves. Journal of Plant Physiology 160, 271–282.

Hepple, R.P., Benson, S.M., 2005. Geologic storage of carbon dioxide as a climate change mitigation strategy: performance requirements and the implications of surface seepage. Environmental Geology 47, 576–585.

Hoeks, J., 1972a. Effect of leaking natural gas on soil and vegetation in urban areas. Agricultural Research Reports. 778.

Hoeks, J., 1972b. Changes in composition of soil air near leaks in natural gas mains. Soil Science 113, 46–54.

Holloway, S., 2005. Underground sequestration of carbon dioxide — a viable greenhouse gas mitigation option. Energy 30, 2318–2333.

Horler, D.N.H., Dockray, M., Barber, J., 1983. The red edge of plant reflectance. International Journal of Remote Sensing 4, 273–288.

Huang, B., Johnson, J.W., Nesmith, D.S., 1997. Responses to root-zone CO_2 enrichment and hypoxia of wheat genotypes differing in waterlogging tolerance. Crop Science 37, 464–468.

IPCC, 2005. In: Metz, Davidson B.O., De Coninick, H.C., Loos, M., Meyer, L.A. (Eds.), IPCC Special Report on Carbon Dioxide Capture and Storage: Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, p. 442.

Jago, R.A., Curran, P.J., 1996. Estimating the chlorophyll concentration of a grassland canopy for chemical monitoring using remotely sensed data. Paper presented at the Remote Sensing and Industry Conference, Remote Sensing Society, University of Nottingham.

Knipling, E.B., 1970. Physical and physiological basis for the reflectance of visible and near-infrared radiation from vegetation. Remote Sensing of Environment 1, 155–159.

Kochubey, S.M., Kazantsev, T.A., 2007. Changes in first derivatives of leaf reflectance spectra of various plants induced by variations in chlorophyll content. Journal of Plant Physiology 164, 1648–1655.

Kumar, M., Monteith, J.L., 1981. Remote sensing of crop growth. In: Smith, H. (Ed.), Plants and the Daylight Spectrum. Academic Press, London, UK, pp. 133–144.

Levitt, J., 1980. 2nd ed. Responses of Plants to Environmental Stresses, vol. 2. Academic Press, New York.

Lichtenthaler, H.K., 1998. The stress concept in plants: an introduction. Annals of New York Academy of Sciences 851, 187–198.

Llewellyn, G.M., Curran, P.J., 1999. Understanding the grassland red-edge using a combined leaf and canopy model. paper presented at the 25th Annual Conference of The Remote Sensing Society 25th: From data to information, University of Cardiff.

Macek, I., Pfanz, H., Francetic, V., Batic, F., Vodnik, D., 2005. Root respiration response to high CO_2 concentrations in plants from natural CO_2 springs. Environmental and Experimental Botany 54, 90–99.

Margalef, R., 1974. Ecologia [Ecology]. Omega, Barcelona.

Marschner, H., 1995. Mineral Nutrition of Higher Plants, 2nd ed. Academic press, New York.

Miglietta, F., Raschi, A., Bettarini, I., Resti, R., Selvi, F., 1993. Natural CO_2 springs in Italy — a resource for examining long term response of vegetation to rising CO_2 concentrations. Plant Cell Environment 16, 873–878.

Milton, M.N., Monat, D.A., 1989. Remote sensing of vegetation responses to natural and cultural environment condition. Photogrammetric Engineering and Remote Sensing 55, 1167–1173.

Moran, J.A., Mitchell, A.K., Goodmanson, G., Stockburger, K.A., 2000. Differentiation among effects of nitrogen fertilization treatments on conifer seedlings by foliar reflectance: a comparison of methods. Tree physiology 20, 1113–1120.

Noomen, M.F., Skidmore, A.K., 2009. The effects of high soil CO_2 concentrations on leaf reflectance of maize plants. International Journal of Remote Sensing 30, 481–497.

Noomen, M.F., Smith, K.L., Colls, J.J., Steven, M.D., Skidmore, A.K., Van Der Meer, F.D., 2008. Hyperspectral indices for detecting changes in canopy reflectance as a result of underground natural gas leakage. International Journal of Remote Sensing 29, 5987–6008.

Penuelas, J., Baret, F., Filella, I., 1995. Semi-empirical indices to assess carotenoids/chlorophyll *a* ration from leaf spectral reflectance. Photosynthetica 31, 221–230.

Penuelas, J., Gamon, J., Freeden, A., Merino, J., Field, C., 1994. Reflectance indices associated with physiological changes in nitrogen and water limited sunflower leaves. Remote Sensing of Environment 48, 135–146.

Pfanz, H., Vodnik, D., Wittmann, C., Aschan, G., Raschi, A., 2004. Plants and geothermal CO_2 exhalations-survival in and adaptation to high CO_2 environment. Progress in Botany 65, 499–538.

Philpot, W.D., 1991. The derivative ratio algorithm: avoiding atmospheric effects in remote sensing. IEEE Transactions in Geoscience and Remote Sensing 29 (3), 350–357.
Pysek, P., Pysek, A., 1989. Changes in vegetation caused by experimental leakage of natural gas. Weed Research 29, 193–204.
Richardson, A.D., Duigan, S.P., Berlyn, G.P., 2002. An evaluation of noninvasive methods to estimate foliar chlorophyll content. New Phytologist 153, 185–194.
Riggs, G.A., Running, S.W., 1991. Detection of canopy water stress in conifers using the airborne imaging spectrometer. Remote Sensing of Environment 35, 51–68.
Russel, E.W., 1973. Soil Conditions and Plant Growth. Longmans, London.
Sims, D.A., Gamon, J.A., 2002. Relationships between leaf pigment content and spectral reflectance across a wide range of species, leaf structures and developmental stages. Remote Sensing of Environment 81, 337–354.
Smith, K.L., Steven, M.D., Colls, J.J., 2004a. Use of hyperspectral derivative ratios in the red-edge region to identify plant stress responses to gas leaks. Remote Sensing of Environment 92, 207–217.
Smith, K.L., Steven, M.D., Colls, J.J., 2004b. Spectral responses of pot-grown plants to displacement of soil oxygen. International Journal of Remote Sensing 20, 4395–4410.
Smith, K.L., Steven, M.D., Colls, J.J., 2005. Plant spectral responses to gas leaks and other stresses. International Journal of Remote Sensing 26 (18), 4067–4081.
Spangler, L.H., Dobeck, L.M., Repasky, K.S., Nehrir, A.R., Humphries, S.D., Barr, J.L., Keith, C.J., Shaw, J.A., Rouse, J.H., Cunningham, A.B., Benson, S.M., Oldenburg, C.M., Lewicki, J.L., Wells, A.W., Diehl, J.R., Strazisar, B.R., Fessenden, J.E., Rahn, T.A., Amonette, J.E., Barr, J.L., Pickles, W.L., Jacobson, J.D., Silver, E.A., Male, E.J., Rauch, H. W., Gullickson, K.S., Trautz, R., Kharaka, Y., Birkholzer, J., Wielopolski, L., 2009. A shallow subsurface controlled release facility in Bozeman, Montana, USA, for testing near surface CO_2 detection techniques and transport models. Environmental Earth Sciences, special issue doi:10.1007/s12665-009-0400-2 Available online at: http://www.springerlink.com/content/92132x1025610407/fulltext.pdf.
Tsai, F., Philpot, W., 1998. Derivative analysis of hyperspectral data. Remote Sensing of Environment 66, 41–51.
Vodnik, D., Kastelec, D., Pfanz, H., Macek, I., Turk, B., 2006. Small-scale spatial variations in soil CO_2 concentration in a natural carbon dioxide spring and some related plant responses. Geoderma 133, 309–319.
Weiss, M.G., 1943. Inheritance and physiology of efficiency in iron utilization in soybeans. Genetics 28, 253–268.
Yang, C.M., Chen, R.K., 2007. Changes in spectral characteristics of rice canopy infested with brown planthopper and leaffolder. Crop science 47, 329–335.
Young, A., Britton, G., 1990. Carotenoids and stress. In: Alscher Jr., R.G., Cumming, J.R. (Eds.), Stress Responses in Plants: Adaptation and Acclimation Mechanisms. Wiley-Liss, New York, pp. 87–112.