Use of hyperspectral derivatives ratios in the red-edge region to identify plant stress responses to gas leaks

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Abstract

Hyperspectral features in the red-edge were tested as an index of plant stress responses to soil-oxygen depletion. The aim was to provide the basis for a warning system to identify natural gas leakage by the spectral responses of plants growing in the affected soil.

Elevated concentrations of natural gas in the soil atmosphere were used to deplete oxygen concentrations around the roots of grass, wheat (*Hordeum vulgare* cv Claire) and bean (*Vicia faba* cv Clipper) growing in a field facility. Visible symptoms due to the natural gas included reduced growth of the plants and chlorosis of the leaves.

Spectral responses included increased reflectance in the visible wavelengths and decreased reflectance in the near infra-red. Derivative analysis identified features within the red-edge at 720-730 nm and 702 nm. Ratios of the magnitude of the derivative at 725 to that at 702 nm were less in areas where gas was present. This ratio enabled identification of stress due to gas leakage 7 days before visible symptoms were observed and also at the edges of gassed plots where visible symptoms were not expressed. This study suggests that remote sensing could be used to detect pipeline gas leaks from decreases in the ratio of peaks within the red-edge.

Introduction

Gas pipeline engineers have reported vegetation changes around the area of gas leaks in underground pipelines. Leaking pipelines may be detected by the use of remote sensing of the surrounding vegetation to identify early signs of plant stress such as chlorosis of the leaves and poor development of the plants. Remote sensing of stressed vegetation by satellite may offer the potential for early detection of symptoms that are below the subjective detection level, while at the same time reducing the risks associated with aerial inspection of the network.

The stress symptoms in response to gas leaks are believed to be a generic response to the displacement of soil-oxygen from the soil, which then inhibits root function (Hoeks, 1972; Gilman *et al.*, 1982; Arthur *et al.*, 1985; Smith, 2002). This effect may be compounded by the oxidation of leaking methane by methanotrophic bacteria that utilise the methane present in natural gas as a carbon-based energy source (Hanson & Hanson, 1996).

Remote sensing has previously been used to detect stress in plants before visible symptoms have been observed. Carter, (1993), Carter and Miller, (1994) and Carter *et al.*, (1996) used various stresses and plant species to induce changes in reflectance and found that visible reflectance increased consistently in response to stress, and that herbicide-induced stress was detectable 16 days prior to the first visible signs of stress. Other authors have used the red-edge wavelength, defined as the wavelength within the range 680 – 750 nm corresponding to the maximum slope in the reflectance (Horler *et al.*, 1983; Filella & Penuelas, 1994). Rock *et al.*, (1988) detected a shift in the red-edge, towards the blue, of approximately 5 nm when measuring severe foliage stress on spruce trees due to air pollution. This shift, which was due to a decline in chlorophyll in the pine needles, was detected before visual symptoms became apparent and it was proposed that airborne monitoring could be used to provide an early indicator of vegetation stress.

The red-edge wavelength can be found by plotting the first derivative of the reflectance spectrum, and then manually identifying the highest peak (Horler *et al.*, 1983; Boochs *et al.*, 1990; Filella & Penuelas, 1994), or by fitting a Gaussian curve to the red-edge and extracting the maximum slope wavelength from the coefficient of the fitted curve (Miller *et al.*, 1990; Pinar & Curran, 1996). A limitation of both techniques is the assumption that there is only a single maximum in the gradient of the red edge (Lamb *et al.*, 2002). Smoothing of hyperspectral reflectance spectra to remove noise is usually carried out prior to derivative analysis and this often has the effect of smoothing out small spectral features that may contain important stress-related information.

Several researchers have shown that the red-edge is actually composed of two or more features. Horler *et al.* (1983) identified two peaks in derivative spectra; the first at around 700 nm was attributed to the chlorophyll content in the plant leaves and the second at around 725 nm was attributed to cellular scattering in the leaf. Boochs *et al.* (1990) identified peaks in winter wheat at 703 and 735 nm and Railyan and Korobov (1993) noticed underlying components in the red-edge situated at 700, 715, and 745 nm. Similar effects were seen in the red-edge of a grass canopy by Jago and Curran (1996) and Llewellyn and Curran (1999). While studying grassland canopies at a site contaminated with oil, Jago and Curran (1996) found maxima within the red-edge with peaks at approximately 709 nm and 693 nm. The position of the major peak changed depending on the amount of contamination within the plot. Llewellyn and Curran (1999) also found multiple first derivative features with peaks at 700 and 729 nm. They found that the shorter wavelength feature indicated grassland with high levels of soil contamination whereas the longer wavelength feature indicated lower levels of contamination; the transition from one red-edge position to another was not a gradual change but instead a switch in dominance of the features. Lamb *et al.,* (2002) found that in leaves with low chlorophyll content the peak at ~705 nm was dominant but with higher chlorophyll levels the peak at

~725 nm was dominant. Zarco-Tejada *et al.,* (2002) found that a double peak in the derivative reflectance spectrum of the red-edge at 705 and 722 nm was related to increased chlorophyll fluorescence and chlorophyll concentration. Changes in chlorophyll function often precede changes in chlorophyll content so that fluorescence changes are often observed before leaves become chlorotic.

Although these features have been identified previously they have not been applied as a method of detecting stress effects that could be used in a remote sensing monitoring system.

In this study three contrasting plant species were exposed to elevated concentrations of natural gas in soil to determine whether gas leaks could be detected by remote sensing. Hyperspectral reflectance spectra were used to identify changes in the spectral response of plants. The shape and position of the red-edge was studied and ratios of derivative peaks used to detect differences between control and gassed plants.

Methods

Site

A soil–gas research facility (18 m x 16 m) was set up in a field of permanent pasture at the Sutton Bonington campus of the University of Nottingham (52.8ºN, 1.2ºW). The soil type lies within the Worcester Series and comprises 30 cm deep sandy clay loam overlying a 70+ cm clay and marl horizon (Reeve, 1975). Eighteen plots (each 2.5 x 2.5 m) were laid out within the experimental area to enable gas to be delivered to different crops. To allow spectral reflectance measurements of vegetation to be made on the plots, the facility was positioned so that it was not influenced by shade from trees or fencing.

Mains gas (at 21 mbar) was delivered via copper tubing to twelve plots (the other six acting as ungassed controls) at a nominal flow rate of 100 l hr^{-1}. To avoid obstructing the measurement area, and to enable overhead spectral measurements to be taken without the gas pipe being in the field of view, the tubing was inserted into augered holes at an angle of 30° to the vertical, such that the gas was delivered into the soil 1 m below the centre of the plot. Gas flow to each plot could be individually regulated and isolated.

Gas measurements

Gas concentration in the soil was measured by means of vertical plastic sampling tubes, perforated at the bottom, installed at distances of 15, 70 and 140 cm from the centre of each plot and at a depth of 50 cm. The soil gas concentration was measured using a Gasurveyor 442 (GMI Ltd, Renfrewshire, Scotland), which measures methane in the ranges 0-1000 ppm and 0-100 % volume, and oxygen in the range 0-25%. Measurements of methane and oxygen concentration were taken daily between 8 and 8.30 am from 1st October 2002.

Plants and treatments

Two experiments were carried out to determine the effect of natural gas, firstly on germinating seeds and secondly on a fully established crop. Three different plant species – grass, winter wheat, and field bean were used in each of six replicate plots. Grass was pre-established at the site, (the field had been re-seeded in 1997 with a perennial rye grass mixture (cv Long Ley) suitable for cutting and grazing), and so six plots were prepared by mowing. The grass plots were mown at approximately two-weekly intervals throughout the study. Winter wheat (*Hordeum vulgare* cv Claire) was sown at a density of 300 seeds m^{-2} in six plots on 30th October 2002; germination commenced on 11th November 2002. Bean (*Vicia faba* cv Clipper) was sown at a rate of 30 seeds m^{-2} into the remaining six plots and germination commenced on 28th November 2002. In the first experiment, gas was delivered to two plots of grass from 1st October 2002 and to two plots of wheat and bean from the time of sowing. On the 12th May 2003 gas was also switched on to two additional plots each of grass, bean and winter wheat to determine the effect of a new gas leak on an established crop. The early-gassed wheat and bean were harvested on 15 May 2003. In the late-gassing experiment, the gas supply was terminated to the wheat and bean on 28th July 2003 and the crops harvested. The late-gassed grass experiment was terminated on 2nd September 2003. The early-gassed grass experiment continued until 9th December 2003. Table 1 outlines the identification, crop and treatment for each plot.

Spectral measurements

Plant stress effects were detected by spectral scanning between 350 and 2500 nm with an ASD Fieldspec FR spectroradiometer (ASD, Boulder, USA) fitted with a fibre optic probe having a 25° field of view. The sampling interval over the 350-1050 nm range is 1.4 nm with a resolution of 3 nm (bandwidth at half maximum). Over the 1050 - 2500 nm range the sampling interval is about 2 nm and the spectral resolution is between 10 and 12 nm. The results are then interpolated by the ASD software to produce readings at every 1 nm. Scans were taken from a height of 60 cm so that the field of view at the ground was 24 cm diameter. Scans were optimised and referenced against a halon panel prior to scanning the vegetation. Scans were taken at 50 cm intervals along a transect laid across each plot. An average of 25 scans was measured at each point. For wheat and bean, scans were taken on sunny days on an approximately weekly basis between 18 March and 28 July 2003. For grass, scans continued until 9 December 2003 to determine the effect of a full year's gassing on the early-gassed grass and to monitor grass recovery in the late-gassed grass following termination of the gas supply on 2nd September.

Spectral analysis

Relative reflectance data were corrected for the absolute reflectance of the halon panel and then smoothed using a weighted mean moving average over a 5 nm sample. It was found that a 5 point weighted average (with relative weights of 0.25, 0.5, 1, 0.5 and 0.25) gave sufficient smoothing without loss of fine spectral detail.

Figure 1 shows smoothed reflectance for control and gassed grass plots. It was difficult to determine differences between reflectance spectra from grass along the transect. Hence, derivative spectra were calculated to provide a more sensitive analysis.

Derivative analysis was used primarily to locate the position and height of the red-edge and other peaks that may indicate stress in plants. The derivative was calculated by dividing the difference between successive spectral values by the wavelength interval separating them. In this case a 2 nm interval was used. The non-uniform weighting scheme used to smooth the data ensured that the derivative calculation is spread across six data points, thus retaining the smoothing effect.

The red-edge peak was composed of a peak maximum between 720 and 730 nm and a smaller peak or shoulder at around 702 nm. These features were used to detect differences between control and gas-stressed plants. A ratio of the magnitudes of the derivative at 725 and 702 nm was calculated.

Studies were also made to determine the effect of gas on the edge of plots where visible symptoms were not observed. For the gassed plots, data from the two inner transect points at 100 and 150 cm were averaged to show the effect of the gas on the centre of the plot, and data from the two outer transect points at 50 and 200 cm were averaged to show the effect of the gas on the edges of the plots. For the control plots, data from all four transect points were averaged.

3 Results and Discussion

Gas concentrations

Elevated levels of natural gas in the soil were achieved but the concentration was variable, both between plots and over time, possibly due to variations in the depth of the soil horizons across the site and the different vegetation types growing in the plots. The mean gas concentration measured in the gas sampling tubes was in the range 2.1 (sd 1.4) to 54 (sd 29)% volume gas in the tubes that were 15 cm from the centre of the plots and significantly less (< 0.01% volume gas) in the tubes at 70 and 140 cm from the centre. Soil oxygen concentration was depleted in plots with elevated levels of natural gas. Mean oxygen concentration was 11.3% (sd 7.7). Average oxygen concentrations below 10% were found in 5 plots and were associated with high concentrations of natural gas (over 20%). Hoeks, (1972) also found almost zero oxygen concentrations, and carbon dioxide concentrations of up to 14%, in soil near a gas leak.

Visible symptoms

Injection of natural gas into soil beneath an established grass crop caused a circle of chlorosis approximately 50 cm in diameter, and reduction in growth of the grass around the area of gas injection. In the early-gas experiment, symptoms of stress were visible in the grass 44 days after gas injection started while in the late gassing experiment symptoms became apparent after only 32 days. In comparison Pysek and Pysek, (1989) found that symptoms were first observed in various species of vegetation between 15 to 30 days after exposure to a leaking gas main and Smith *et al.,* (2004) found that decreased soil oxygen caused stress effects in pot-grown barley and bean between 14 and 21 days after starting treatment.

Injection of natural gas into the soil in which bean and winter wheat were growing reduced growth of the seedlings and discoloured leaves but symptoms were not seen until early March 2003 (a period of more than 4 months) at the time when the plants were beginning to grow after the winter months. Hoeks, (1972) found that the first symptoms of injury to trees caused by gas leaks were observed 1 to 3 months after the start of the gas leakage. In the area of soil with the greatest gas concentration most plants had germinated but they did not grow subsequently. The patches of decreased growth were generally 0.5 to 1 m diameter, and were within the area of highest gas concentration which was consistent with the work of Scholenberger, (1930) and Godwin *et al.*, (1990).

In the late-gassing experiment, when gas was delivered to wheat and bean plants with full canopies, no visible symptoms were observed. It has been suggested that the main damaging effect of elevated levels of natural gas on plant growth is due to the displacement of soil oxygen thus inhibiting root respiration that provides energy for root growth and uptake of water and nutrients from the soil (Adamse *et al.*, 1971; Hoeks, 1972; Gilman *et al.*, 1982; Arthur *et al.*, 1985; Smith, 2002). The root system of wheat and bean was probably fully developed by the time that the gas was switched on in the late experiment. Roots of wheat and bean can extend downwards to 1 m depth but due to the thick clay layer beneath the loam on our site, most roots probably grew down through the loam and then extended sideways throughout the plot, so that water and nutrients were obtained from areas of the soil that were unaffected by gas.

Spectral data

Measurements showed that vegetation exposed to the highest concentrations of natural gas in the soil had increased reflectance in the visible and decreased reflectance in the infrared. Figure 1 illustrates this response with reflectance measurements for a control grass plot and an early-gassed grass plot taken on the same day. Other researchers have identified similar responses to a wide range of plant stresses including waterlogging, nutrient stress, heavy metal toxicity and soil oxygen deficiency (Wooley, 1971; Horler *et al.*, 1983; Milton *et al.*, 1989; Carter, 1993; Carter & Miller, 1994; Anderson & Perry, 1996; Smith *et al.*, 2004). In most cases changes in spectra tend to be a generic response to stress induced changes in chlorophyll concentration.

Derivative analysis showed that the red-edge (680-750 nm) was comprised of an asymmetric peak with several secondary features. In the control plots the shape of the red-edge did not vary along the transect but it was possible to identify two distinct features within the peak. The main peak was located between 720 and 730 nm and a smaller peak or shoulder could be seen at 702 nm. In the gassed plots there was a change in position and magnitude of the main peak along the transect and the secondary peak at 702 nm became more prominent. Other minor features were also observed at 720 nm and 735 nm. Figure 2 illustrates these changes in the first derivative, showing the red-edge position for control and early-gassed grass plots. Similar results were observed for early-gassed wheat and bean. Other researchers have also found similar features. Railyan and Korobov, (1993) found peaks at 705 and 720 in the vegetative state of *Triticale* and Boochs *et al.*, (1990) working with winter wheat found a minor peak at 703 nm and a dominant peak that averaged 735 nm but varied between 725 and 740 nm throughout the growing season. Horler *et al.*, (1983), Miller *et al.*, (1991) and Filella and Penuelas, (1994) identified peaks at around 700 and 725 in various species and Zarco-Tejada *et al.*, (2003), investigating potted trees of *Acer negundo* subjected to temperature and humidity stress, observed peaks at 705 and 722 nm.

Ratios of the magnitude of the derivative at 725 and 702 nm were calculated to determine if changes in these wavelengths could be related to elevated soil gas concentration. The peak at 702 nm was used as this peak was the most stable in wavelength and changed only in magnitude throughout the season. The major peak within the red-edge varied between 720 and 730 nm and so 725 nm was chosen as a mean value. These values are consistent with those observed by other authors (Horler *et al.*, (1983)., Miller *et al.*, (1991) and Filella and Penuelas, (1994)). Smith (2002) studying barley that had been grown above a leaking gas pipe also identified features within the red-edge at 725 and 702 nm, but not the finer features at 718 or 735 nm. Smith’s measurements were made with a LI-COR 1800 spectroradiometer (LI-COR Inc, Nebraska, USA), which has a spectral resolution of 4 nm. The choice of derivative features at 725 nm and 702 nm thus offers a ratio index that is less instrument dependent as these features are also identifiable with instruments that have a lower specification than the ASD Fieldspec Pro.

It was observed that in the early-gassed plots the ratio decreased by 30 to 50% in the scans taken at 100 and 150 cm along the transect ($p < 0.01$). This was the area where the concentration of natural gas was highest. Figure 3 shows the change in this ratio along the transect for early-gassed grass, wheat and bean. A similar response was observed for the late-gassed grass where a decrease of 24% was observed in the ratio on 9th June 2003 ($p = <0.01$). This was 25 days after gas had been switched on to the late-gassed plots and one week before visible symptoms were observed in the grass. However, in the late-gassed plots of wheat and bean there was no decrease in the ratio, which is consistent with the lack of visible symptoms and suggests that at this late stage of plant development the elevated soil gas concentration had no stress effect.

The seasonal evolution of derivative ratio was plotted to give an indication of how the ratio changes as the crop develops (figure 4). In all species the ratio of first derivatives at 725 and 702 nm increased as the crop developed but for early-gassed plants the ratio was consistently lower than in the control plants. The ratio is partly sensitive to the amount of soil visible within the scan area. However, over the wavelength range of the red edge the change in reflectance from soil is significantly smaller than the change in reflectance from vegetation (about 10%) and a sensitivity analysis indicates that as long as vegetation cover is greater than about 20% the effect of soil background on the derivative ratio will be small. Decreases in the ratio were observed from early March (when scanning began) despite low ground cover at that time. Horler (1983) also suggested that field measurements of the red-edge position would be unaffected by the amount of ground cover, providing that the red-edge remains measurable. However, when the gas was switched on after development of a full canopy (late-gassing), there was no change in the ratio for bean and wheat and the ratio continued to be consistent with that obtained from control plots. The effect of late-gassing on grass was to reduce the ratio until it became equivalent to the ratio for early-gassed grass. When the supply of gas was terminated to the late-gassed plots (Plots C and E) on September 2nd 2003, the ratio remained low for 6 weeks before slowly increasing as the grass recovered. Hoeks (1972) similarly found a slow recovery of vegetation following the repair of a gas leak. He suggested that it could take one to two months for the oxygen consumption rate of the gassed soil to reach a level similar to that of an ungassed soil due to the presence of intermediary breakdown products during bacterial oxidation of methane, and that the whole recovery process could take up to a year.

Studies of edge effects in the gassed plots showed that the ratio for the centre of the gassed plots was lower than the ratio for the controls, and the ratio from the edge of the gassed plots was intermediate between those obtained from the centre of the gassed plot and from the control. This suggests that although symptoms were not visible at the edges of the gassed plots the gas caused a stress effect that was detectable by remote sensing. Figure 5 shows the results for early-gassed bean. Similar results were seen for early-gassed wheat and early and late-gassed grass. Zarco-Tejada *et al.*, (2002; 2003) similarly found that a double peak in the derivative reflectance could indicate stress conditions, which they attributed to low chlorophyll content and chlorophyll fluorescence. Fluorescence occurs when red and far-red light is emitted from green plants in response to excess stimulation by photosynthetically active radiation. In general fluorescence is low when photosynthesis is high but increases under stress conditions when the photosynthetic system is unable to respond effectively to light. Chlorophyll fluorescence is at a maximum near 690 and 730 nm (Lichtenthaler, 1996; Zarco-Tejada *et al.*, 2002). Changes in chlorophyll function often precede changes in chlorophyll content; hence chlorophyll fluorescence changes are often observed before leaves become chlorotic, which may explain the decrease in the ratio at the edge of the gassed plots even though there were no visible symptoms.

4 Conclusions

Elevated concentrations of natural gas in the soil caused stress in grass, bean and wheat, which was manifest as decreases in growth and chlorosis of the leaves. Stress was detected in gassed plants using a ratio of the derivative of the features in the red-edge at 725 and 702 nm. In grass this ratio detected the stress at least 7 days before visible symptoms were observed. The ratio was also capable of detecting responses on the edges of the gassed plots even when no visible symptoms were noted. This ratio appeared to be relatively insensitive to the amount of ground cover and was able to distinguish between gassed and ungassed vegetation from early plant establishment. However, remote sensing was most able to detect stress caused by elevated soil gas concentrations when the root and shoot growth were beginning as seen in the early-gassed wheat and bean. Plants are more sensitive to anaerobic conditions during early growth stages than during the winter when metabolic activity of the roots is low (Hoeks 1972). In our study symptoms were seen in grass at around 40 days and continued throughout the study as the roots were continually growing in the upper levels of the soil where the effect of oxygen depletion was greatest. Wheat and bean were only affected in the spring when the root and shoot growth were beginning. When gas was delivered to wheat and bean that had developed a full canopy there was no effect, probably because the plants had developed a full root system by that stage so that the roots were able to obtain nutrients and water from regions outside of the zone of influence of the gas. Grass was probably more sensitive to elevated gas concentrations because of its shallower root growth and the additional stress effect of mowing.

Although the presence of elevated levels of soil-gas was detected, the symptoms are believed to be a generic response to depleted soil-oxygen. A definitive value for the derivative ratio that could indicate a gas leak was not identified as the ratio values changed throughout the season, and elevated soil gas concentration could only be detected by comparison with ungassed vegetation. However, it is suggested that the derivative ratio might also be suitable for identifing other areas of soil-oxygen depletion such as areas of waterlogging or soil compaction.

These results suggest that it could be possible to detect gas leaks using remote sensing. Using pipeline maps, comparisons of vegetation along the pipeline could be made with neighbouring areas and alarms sent to field investigators when the ratio on the pipeline fell significantly below that of the surrounding vegetation. However, vegetation change due to gas leakage is likely to be slow in developing; and so remote sensing is more suitable for detecting prolonged leaks in isolated regions rather than as an early warning system. Further investigations need to be carried out to determine if hyperspectral ratios could be used in airborne situations for monitoring pipelines.

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Figure Captions

Figure 1 Reflectance of grass measured panel on 14th April 03. (i) represents control grass and (ii) represents early-gassed grass. Each line represents the reflectance from the grass at 50 cm, 100cm etc along the transect. The gaps in the spectra are noisy regions affected by atmospheric water vapour.

Figure 2 First derivative of reflectance of grass plots on 14th April 03. (i) control grass and (ii) early-gassed grass. Each line represents the first derivative of reflectance from the grass at 50 cm, 100cm etc along the transect.

Figure 3 Ratio of derivatives at 725 and 702 nm. (i) grass plots, (ii) s bean and (iii) wheat. Each control is an average of 4 plots and gassed is an average of 2 plots. The data were collected on 8th May 03. The bars indicate standard errors.

Figure 4 Temporal changes in ratio of first derivatives at 725:702 nm, showing effect of early and late gassing. (i) grass, (ii) bean, (iii) wheat. Data collected throughout 2003.

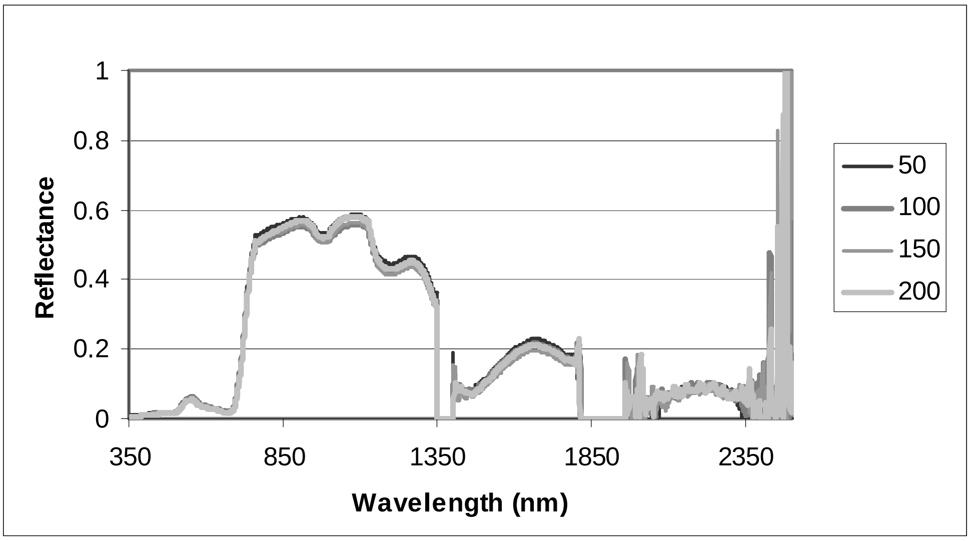
Figure 5 Effect of gas on the centre and edge of early-gassed bean plants. Control plots show means of 8 samples, Gassed Early Centre show means of 4 samples from the 100 and 150 cm transect positions and Gassed Early Edge show mean of 4 samples from the 50 and 200 cm transect positions. The bars represent standard errors.

Tables

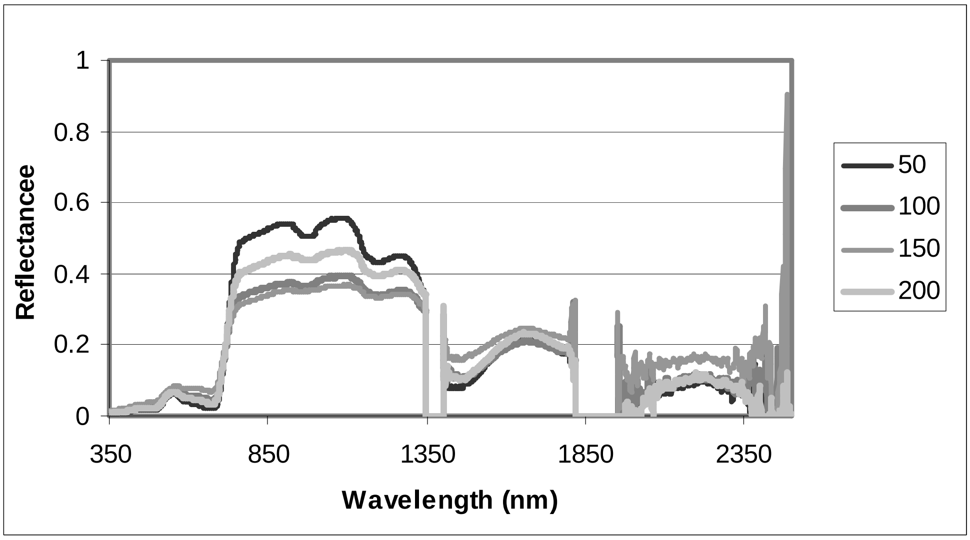
Table 1 Crop, treatment and timing of study.

Crop	**Treatment**	**Date Treatment commenced**	**Date Treatment terminated**
Grass	Control		
Grass	Gassed Early	1st Oct 2002	9th Dec 2003
Grass	Gassed Late	12th May 2003	2nd Sept 2003
Bean	Control		
Bean	Gassed Early	30th Oct 2002	15th May 2003
Bean	Gassed Late	12th May 2003	28th July 2003
Winter wheat	Control		
Winter wheat	Gassed Early	30th Oct 2002	15th May 2003
Winter wheat	Gassed Late	12th May 2003	28th July 2003

Figures

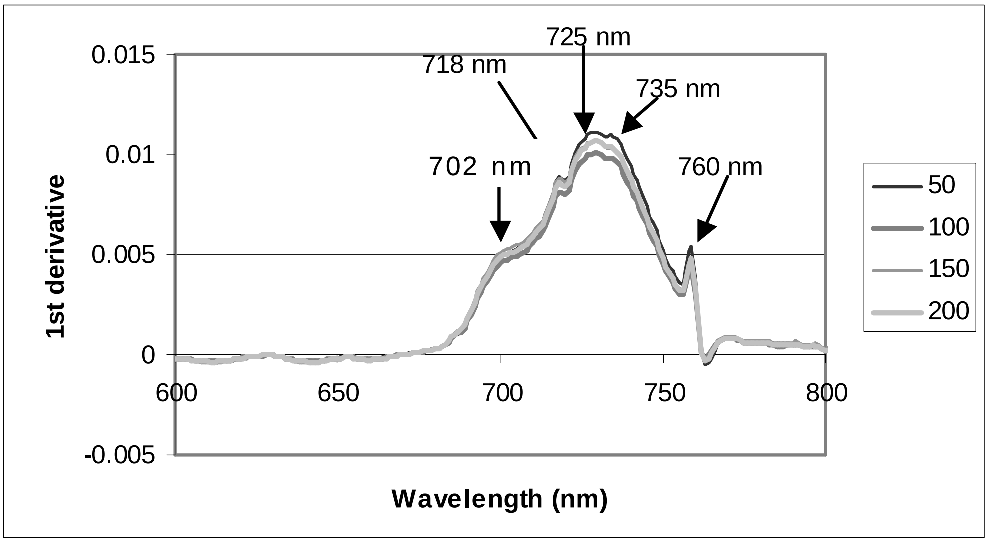


(i)

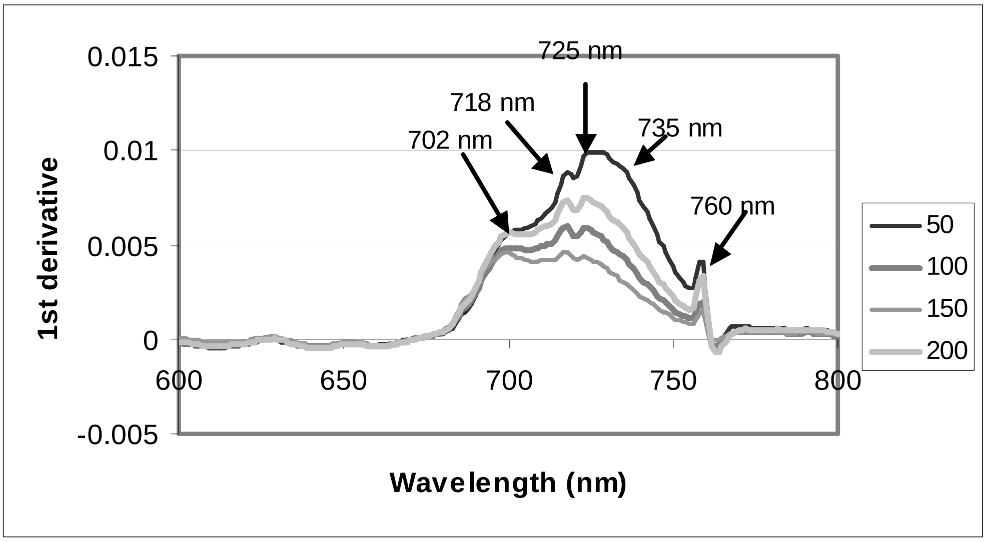


(ii)

Figure 1 Reflectance of grass measured panel on 14th April 03. (i) represents control grass and (ii) represents early-gassed grass. Each line represents the reflectance from the grass at 50 cm, 100cm etc along the transect. The gaps in the spectra are noisy regions affected by atmospheric water vapour.



(i)



(ii)

Figure 2 First derivative of reflectance of grass plots on 14th April 03. (i) control grass and (ii) early-gassed grass. Each line represents the first derivative of reflectance from the grass at 50 cm, 100cm etc along the transect.

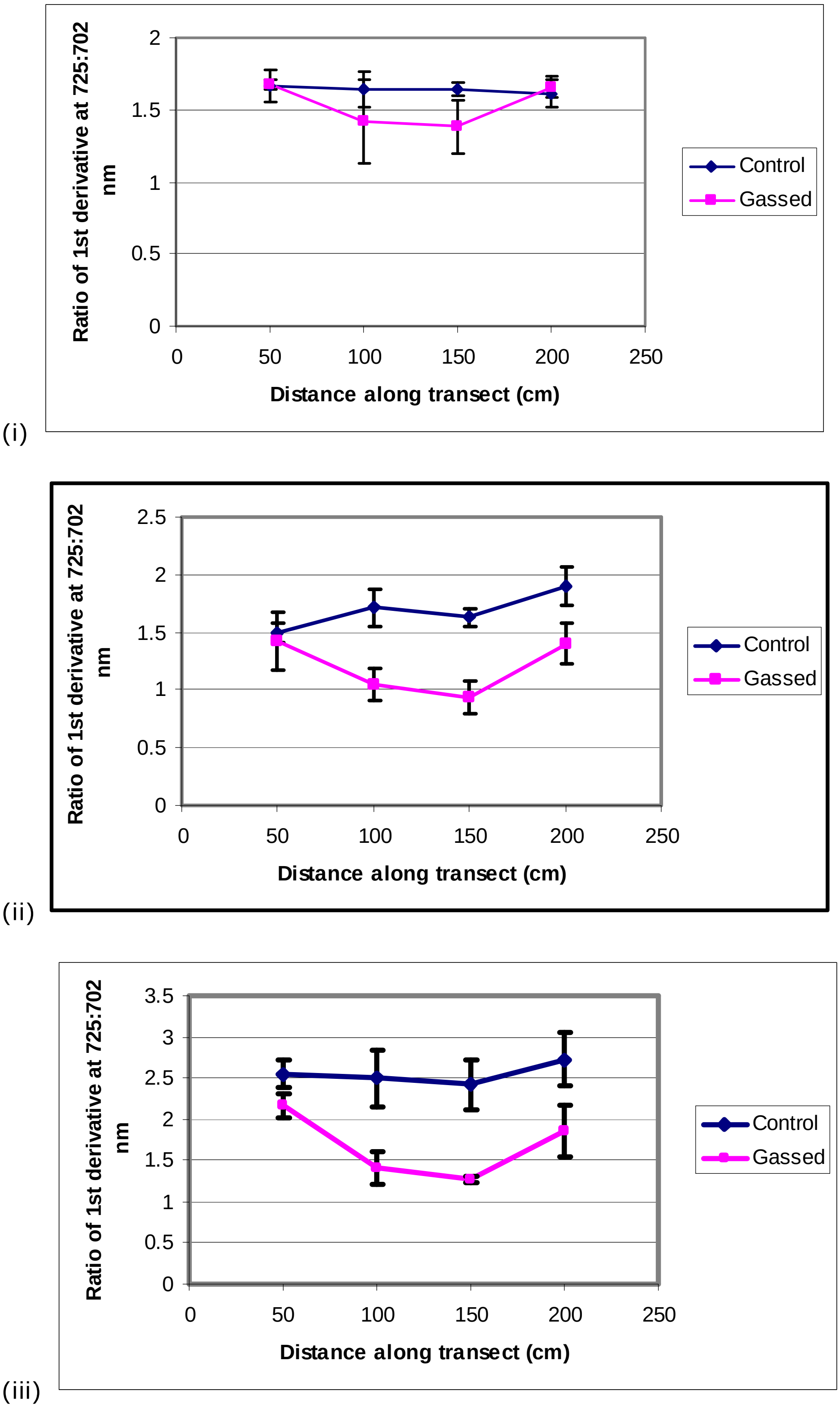
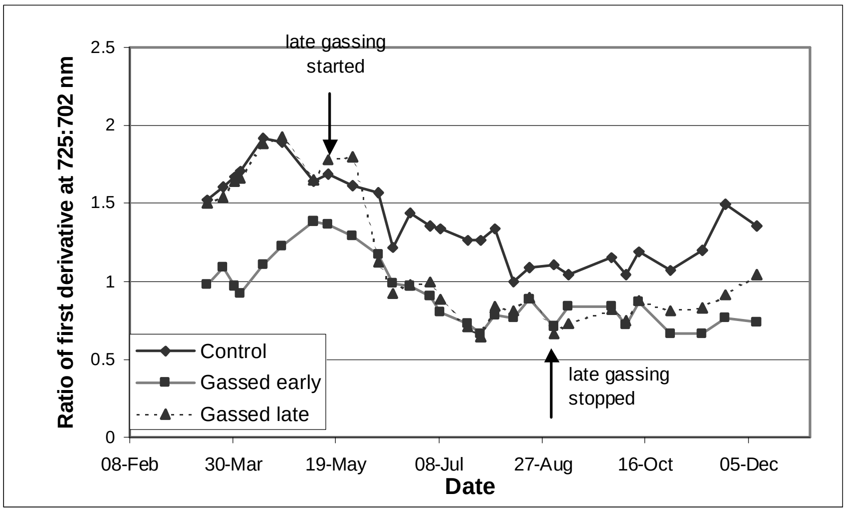
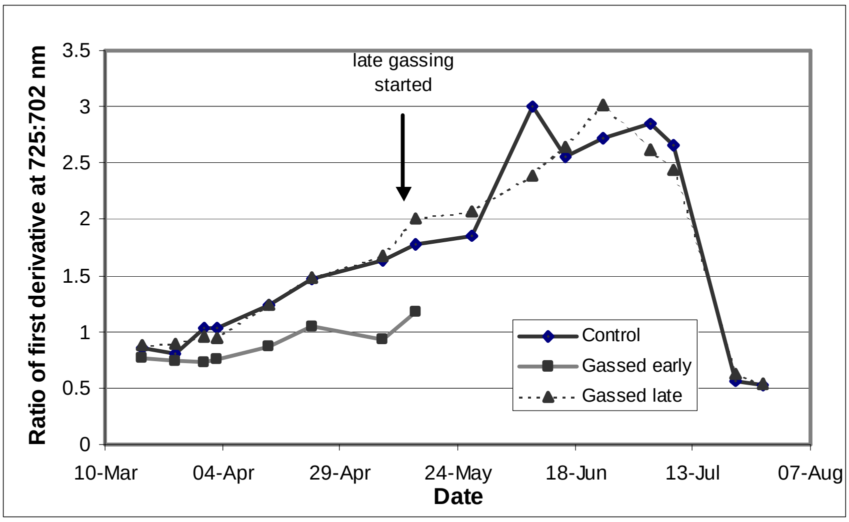


Figure 3 Ratio of derivatives at 725 and 702 nm. (i) grass plots, (ii) s bean and (iii) wheat. Each control is an average of 4 plots and gassed is an average of 2 plots. The data were collected on 8th May 03. The bars indicate standard errors.

(i)



(ii)



(iii)

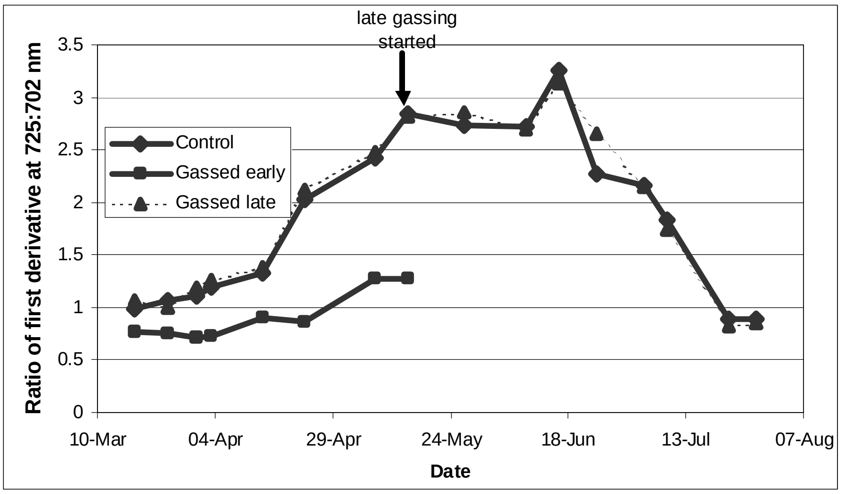


Figure 4 Temporal changes in ratio of first derivatives at 725:702 nm, showing effect of early and late gassing. (i) grass, (ii) bean, (iii) wheat. Data collected throughout 2003.

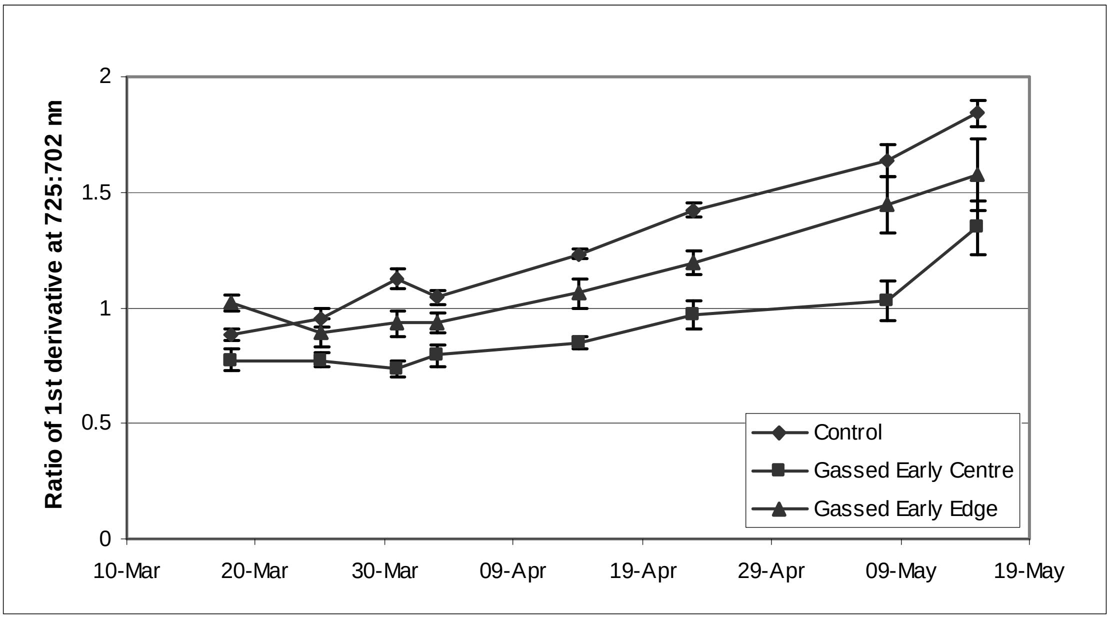


Figure 5 Effect of gas on the centre and edge of early-gassed bean plants. Control plots show mean of 8 samples, Gassed Early Centre show means of 4 samples from the 100 and 150 cm transect positions and Gassed Early Edge show means of 4 samples from the 50 and 200 cm transect positions. The bars represent standard errors.