Plant responses to simulated carbon capture and transport leakage: the effect of impurities in the CO_2 gas stream.

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Running Title

Impurities in the CO_2 gas stream

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Abstract To deliver an effective transition from a carbon-based to a carbon-free energy market, bridging technologies are required. One such possibility is the use of carbon capture and storage, (CCS). However, before such innovations can be rolled out a key requirement is to understand the environmental impact of these technologies. Recent experimental work has demonstrated that small scale CO_2 leakage from CCS pipeline infrastructure has a localised and possibly transient impact. However, what remains unknown is the possibility of synergistic impact of impurities in the CO_2 gas stream. Here we report the impact of two impurities SO_2 (100 ppm SO_2 in pure CO_2) and H_2S (80ppm H_2S in pure CO_2) on the growth and performance of two crop species (spring wheat, *Triticum aestivum* and beetroot, *Beta vulgaris*) in fully replicated experiments. Our data show that when compared to CO_2-only gassed controls, the impact of these impurities are minimal as there are no statistically significant differences between performance parameters (photosynthesis, stomatal conductance and transpiration) or biomass. These results signify that from a plant health perspective it may not be necessary to completely remove these specific impurities prior to CO_2 transportation.

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Introduction

Many high CO_2 emitting industries (e.g. power stations) in the UK are distant from potential carbon storage sites (offshore geological reservoirs) and therefore an infra-structure of CO_2 transportation must be initiated to carry the CO_2 to safe storage. As such there is a need to understand the risks involved and mitigation of potential leaks associated with CCS and dense-phase CO_2 transportation networks into the environment. Recent experimental work has highlighted that the effects of CO_2 leakage on vegetation are highly localised (e.g. Zhou et al., 2013, Sharma et al., 2014, see Smith et al., 2016) and transient with recovery of vegetation close to complete after 12 months (Smith et al., 2016) and that stress is induced by direct CO_2 exposure in addition to a function of O_2 depletion (Lake et al., 2016).

There are, however, two largely unresolved issues; firstly is the role played by both soil type and soil structure in mitigating and/ or enhancing observed plant stresses and secondly, the effects of impurities such as SO_2 and H_2S that may be present in the CO_2 gas stream. Here we address the second issue namely that of impurities in the gas stream.

Impurities in the CO_2 gas stream are a consequence of the specific combusted fuels and capture technologies (Porter et al., 2015). Impurities not only act on the transport properties of the gas stream (Skaugen et al., 2016) but in the event of leakage into the soil environment, will impact on vegetation (including crop plants) growing above the pipeline. The range of impurities and potential concentrations within a pure CO_2 gas stream include both biologically toxic and non-toxic compounds all of which can impact on transportation processes. Non-toxic impurities include H_2O and O_2 (Brown et al., 2014, Porter et al., 2015) and are not detrimental to plants at normal levels in the soil. However, some are known to adversely affect vegetation e.g. SO_x and NO_x when present in atmospheric pollution. Atmospheric loading of these gases reduces the ability of plants to tolerate other abiotic stress factors. For example, the freezing tolerance of heather (*Calluna vulgaris*) is adversely affected by long-term experimental fumigation of SO_2 (plus NO_2) at a concentration of 40 nl l^{-1} (40 ppb) (Caporn et al., 2000); and when *in situ* tolerant plants surrounding a lignite-based thermal power station in the Chennai region of India were monitored for chlorophyll, water content and pH of leaves under constant SO_2 values of 13 to 18 $\mu g\ m^{-3}$ (13 to 18 ppb) (Govindaraju et al., 2012), all three parameters were reduced suggesting that stress is experienced under constant air pollution associated with coal combustion. H_2S has been studied more extensively and is now thought to be involved in biochemical signalling in plants, primarily by priming the biochemical defence responses to abiotic stress, comprehensively reviewed by Lisjak et al., (2013).

Studies specifically involving the soil or root environment are very few in this particular context, Christou et al. (2013) demonstrated the priming ability in strawberry to enhance tolerance to salt stress by subjecting roots to H_2S treatment in hydroponic systems. They found no effect of H_2S on chlorophyll fluorescence, stomatal conductance or water content of leaves compared to non-treated controls, while Cheng et al. (2013) found beneficial effects of H_2S for root protection during extreme hypoxia events in *Pisum sativum*, again in hydroponic systems.

To date there have been no studies into the effects on vegetation of SO_2 and H_2S as components in a CO_2 gas stream delivered directly into the soil environment. To address these knowledge gaps we build on recent experimental protocols (Lake et al., 2016) to test for differences in plant stress as a function of impurities within a pure CO_2 stream.

Materials and methods

Experimental setup

Soil chambers were constructed of acrylic plastic with pipe inlets to allow CO_2 gassing of the soil environment exclusively. The experimental system was housed in a controlled environment growth facility (UNIGRO, UK) to standardise the following environmental variables: irradiance was 300 μmol m^{-2} s^{-1} (at plant height), day/night as 12/12 hours; temperature 21/18°C; and relative humidity 60%. Gas was supplied from either an integral supply (pure CO_2) or a gas cylinder and separated prior to entering each individual soil chamber by two flow rate step-down manifolds. Gas was delivered to each individual chamber at a rate of 30 (±15) mL min^{-1} to maintain CO_2 at steady state. Gases were exhausted to the atmosphere via a separate manifold to prevent build up within the growth room. In all experiments gas concentrations (CO_2 and O_2) were measured daily using the GEOTECH GA5000 gas analyser (Geotech, Warwickshire, UK).

CO_2 impurities

To examine the specific effects that impurities within the CO_2 stream may have on plant responses to simulated CCS leakage certified custom gas mixes were used (manufactured and supplied by BOC, UK). The effect of SO_2 was studied using a mix of 100 ppm SO_2 in pure CO_2 and H_2S using 80ppm H_2S in pure CO_2. These values were derived as midrange values for these impurities present in the gas stream from different carbon capture technologies

(Table 1). To test for specific effects of the impurities, treatment plants (CO_2 + SO_2 or CO_2 + H_2S) were compared to treatment CO_2- only gassed control plants.

Crop species

Crop plants used were spring wheat (*Triticum aestivum* v Tybault - a monocotyledon, grass) and beetroot (*Beta vulgaris* v Pablo F1 - a dicotyledon, vegetable). Crops were sown and grown in Levington's no. 3 multipurpose compost within an environmental controlled growth room (details above) for 1 to 2 weeks before being transplanted into the soil chambers. They were then left to allow sufficient root growth before gassing commenced (approximately 2 weeks later). The gassing period lasted for up to 5 days. After that time, plants become pot-bound which affects physiology and no longer reflects field conditions, hence the experiment was terminated. : Replication consisted of four control plants gassed with CO_2 and six plants gassed with CO_2 + H_2S and six plants gassed with CO_2 + SO_2.

Biomass (shoot)

Plants were harvested between and at the end of each experiment. All shoots (leaves and stems) were taken from each plant, weighed, then dried at 80° C for 2 days and re-weighed. Biomass was measured as fresh and dry weight.

Plant gas exchange

Gas exchange parameters (photosynthesis (A), stomatal conductance (g_s) and evaporation (E) are a measure of plant performance under experimental conditions and determines both the ability of plants to acquire carbon and the rate of simultaneous water loss. Measurements were made using a Li-Cor 6400x IRGA (Li-Cor Inc, Lincoln, Nebraska, USA) on each replicate plant prior to and then daily during gassing until harvest.

Soil pH

Samples were dried at 40 ± 4°C and pH determined following the method of Taylor et al., (2005).

All statistical analyses were carried out using Minitab v 12 (USA). Student's t-tests of each treatment from each other (comparison of means).

Results

CO_2 concentrations

Comparisons between impurity plus CO_2 experiments and pure CO_2 experiments indicate that levels of CO_2 and O_2 are similar across all experiments (Table 2).

Biomass

Fig 1 shows the biomass measurements of wheat (A & B) and beetroot (C & D) when compared to CO_2 gassed control plants. In all measured parameters there is no statistically significant additional effect of added impurities compared to CO_2 gassed controls.

Gas exchange

Fig 2 shows gas exchange parameters (*A*, g_s and *E*) of wheat and Fig 3 of beetroot compared to CO_2 gassed controls. All parameters are affected within the first day of gassing manifested as a dramatic reduction. Photosynthetic rate (*A*) is less affected than both *gs* and *E*. Species differences are apparent with SO_2 causing greater reductions on *A* in wheat than H_2S while H_2S has a greater effect on *A* than SO_2 on *A* in beetroot. Although there are no significant differences between CO_2 gassed control plants and those with added impurities, Table 3 more clearly illustrates the differences in response of each species when the effect of impurities is calculated as a % of CO_2-gassed control plants. Both respond with a slight decrease in overall biomass with addition of H_2S (black outline), while plant performance parameters are differentially affected; wheat is adversely affected by SO_2 (dashed outline) and beetroot by H_2S (black outline). Fig 4 shows the correlations of stomatal conductance (A), transpiration rate (B) and photosynthetic rate (C) with CO_2 concentrations during each experiment. There is a much stronger correlation with CO_2 concentration and both g_s and *E* (water loss) than with *A* (carbon gain).

Soil pH

Table 4 shows the pH of soil prior to growing plants and the experimental treatments along with post-gassing (experimental end). In all cases, the pre-gassed compost is significantly more acidic than with plants and gasses ($p = <0.01$, Student's t-test of means). Soil in the wheat experiment with SO_2 added is significantly more acidic than with CO_2 alone ($p = 0.013$, Student's t-test of means).

Discussion

CO_2 concentrations (and O_2-depletion) are comparable for both sets of experiments. As the impurities are mixed within the CO_2 gas stream, uniformity of impurity is delivered throughout. Biomass data is consistent with previous studies of CO_2 gassing alone (Lake et al., 2016a) and provides evidence that there is no additional effect on productivity when SO_2 or H_2S are present within the CO_2 gas stream. Gas exchange data suggest the mechanism as a disruption to water relations measured as g_s and E as evidenced by much stronger correlations between CO_2 concentration and both g_s and E (water loss) than with A (carbon gain) (Fig 4). This is commensurate with previous studies using this system which demonstrated that the main effect of CO_2 gassing is to reduce stomatal conductance with consequent loss of stomatal control (Lake et al 2016b). However, again there is no additional effect from impurities added to the CO_2 gas stream. While all gas exchange parameters are considerably reduced under CO_2 gas alone compared to non-gassed plants (Lake et al 2016a), species responses to each impurity are evident. Table 3 shows the % change in plants under CO_2 + SO_2 and CO_2 + H_2S from CO_2 gassed control plants. Although the changes are small, and not statistically significant, when calculated as % change SO_2 shows slight increases in biomass measurements, compared to H_2S which shows slight decreases. Gas exchange parameters are reduced under SO_2 in wheat, whereas they are reduced under H_2S in beetroot. This suggests that different stress mechanisms may be employed by different species in response to different impurities and importantly that all impurities cannot be assumed to produce the same results.

Soil pH (Table 4) of the compost before adding the crop plant and prior to gassing is significantly lower than after the experiments illustrating the ability of plants to influence their soil environment and raise pH to a more favourable level. Plants achieve this by producing root exudates to counter or increase acidity dependent on soil conditions as well as influence interactions with other organisms (Wang et al., 2016, Sarker & Karmoker 2016, Bais et al., 2006). Only under CO_2 + SO_2 in wheat does the soil become significantly lower in pH than CO_2 gassing alone, however, this is still above the pH of pre-gassed compost, and did not translate into any additional impact on biomass.

Conclusions

For the first time our data demonstrate that trace amounts of impurities SO_2 and H_2S in pure CO_2 that are likely to be entrained within a CCS CO_2 stream have a negligible impact on plant functional biology (at least under these experimental conditions) when compared to plants exposed to pure CO_2. Therefore these data imply that from a plant health perspective it may not be necessary to completely remove these specific impurities at concentrations tested prior to transportation.

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Figure legends:

Figure 1. Growth characteristics of wheat grown with CO_2 + SO_2 (A), CO_2 + H_2S (B) and beetroot grown with CO_2 + SO_2 (C), CO_2 + H_2S (D) compared to pure CO_2 control after 4 to 5 days treatment. Wheat: leaf height, leaf no., tiller no., fresh weight and dry weight of all top growth (leaf material) and % moisture of all top growth. Beet fresh weight and dry weight of all top growth (leaf material) and % moisture of all top growth [n= 4 to 6, bar = SEmean].

Figure 2. Comparison of time course gas exchange measurements for wheat treated with CO_2 (control) or CO_2 + impurity (SO_2 or H_2S). Stomatal conductance (g_s), transpiration rate (*E*) and photosynthetic rate (*A*) pre-gassing (day 0) and subsequent daily measurement during gassing. [n = 4 or 6, bar = SEmean].

Figure 3. Comparison of time course gas exchange measurements for beetroot treated with CO_2 (control) or CO_2 + impurity (SO_2 or H_2S). Stomatal conductance (g_s), transpiration rate

(*E*) and photosynthetic rate (*A*) pre-gassing (day 0) and subsequent daily measurement during gassing. [n = 4 or 6, bar = SEmean].

Figure 4. Correlations of gas exchange parameters with CO_2 concentration. All individual points inclusive of CO_2 control and CO_2 + impurities. (A) Stomatal conductance; $R^2 = 0.79$; (B) Transpiration rate; $R^2 = 0.84$; (C) photosynthetic rate $R^2 = 0.38$; (Solid line is the linear regression and the dotted line the 95% confidence intervals around the regression, n = 10)

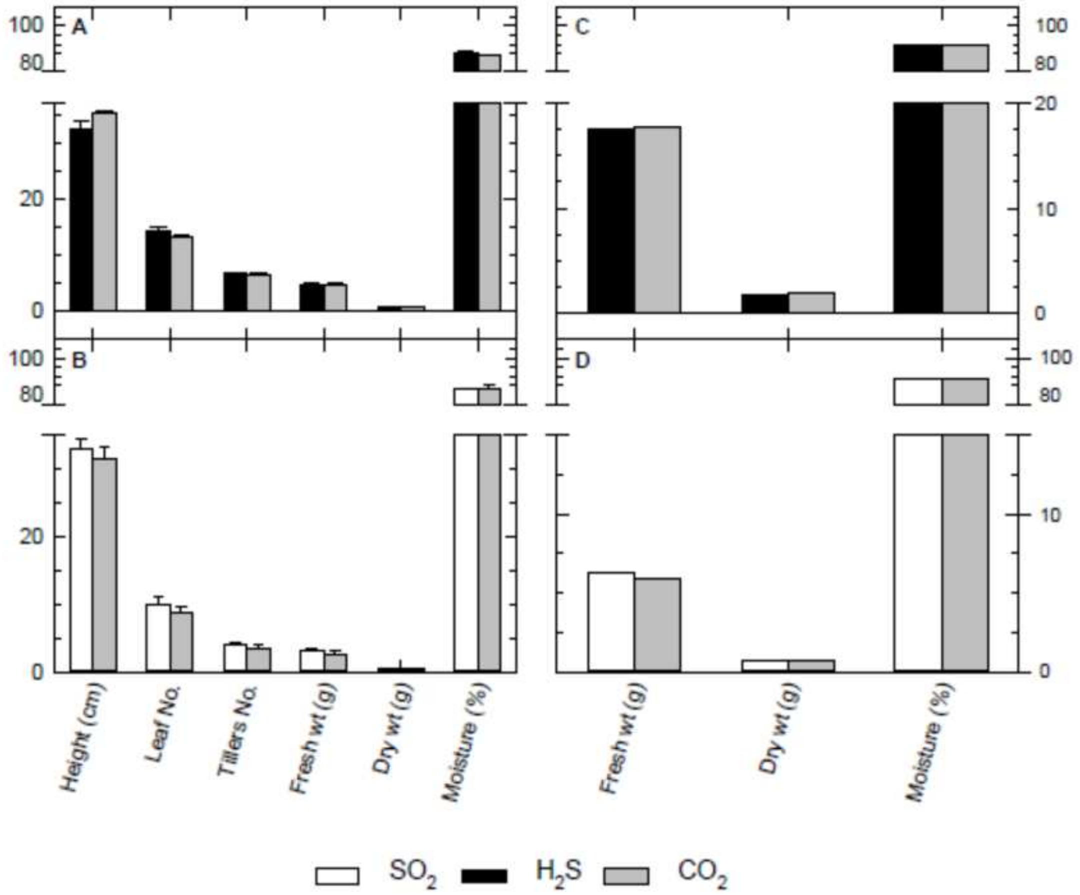
A
B
C
D
100
80
20
0
10
Height (cm)
Leaf No.
Tillers No.
Fresh wt (g)
Dry wt (g)
Moisture (%)
SO₂
H₂S
CO₂

Figure 1

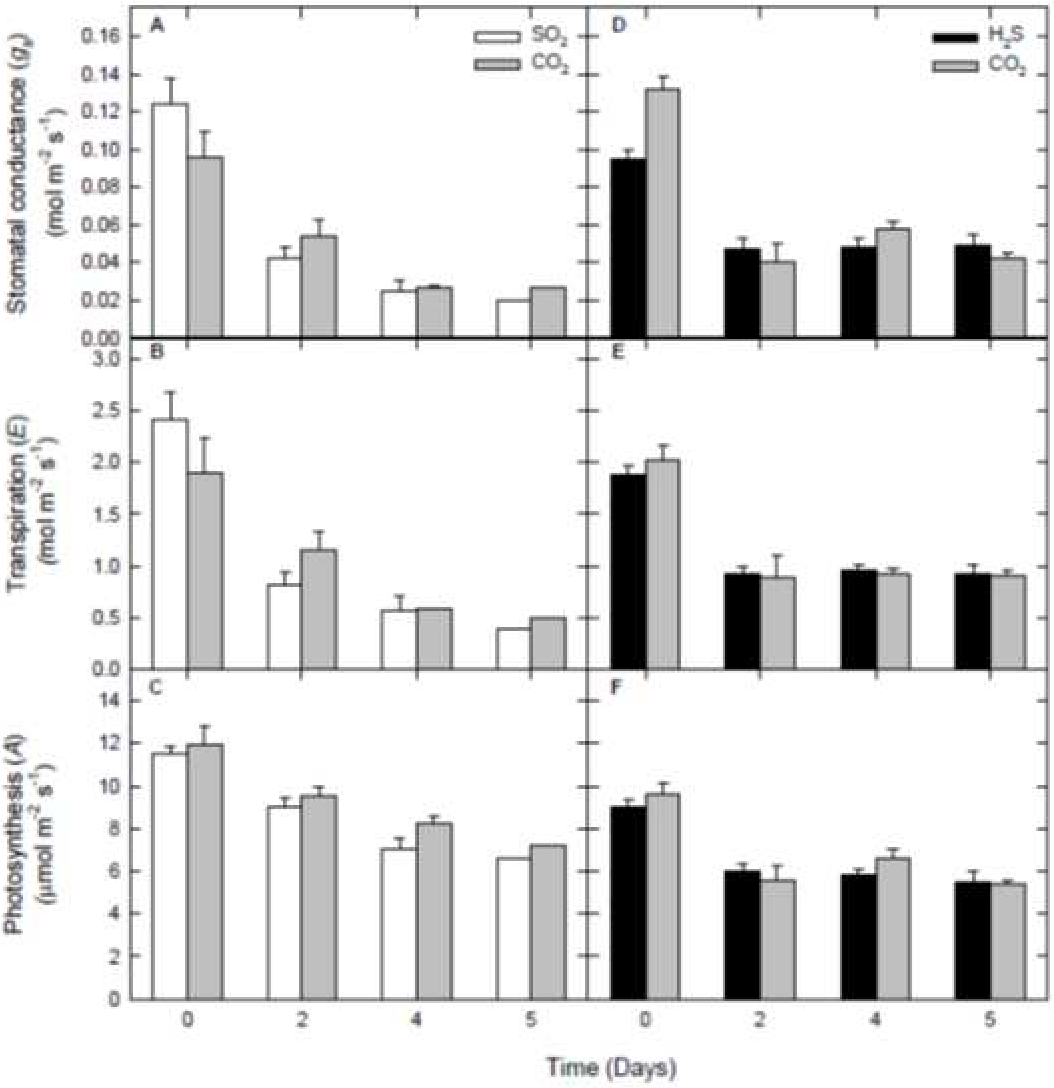
A
B
C
D
E
F
SO$_2$
CO$_2$
H$_2$S
CO$_2$
Stomatal conductance (g_s) (mol m^{-2} s^{-1})
Transpiration (E) (mol m^{-2} s^{-1})
Photosynthesis (A) (µmol m^{-2} s^{-1})
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
2
4
6
8
10
12
14
0
2
4
5
0
2
4
5
Time (Days)

Figure 2

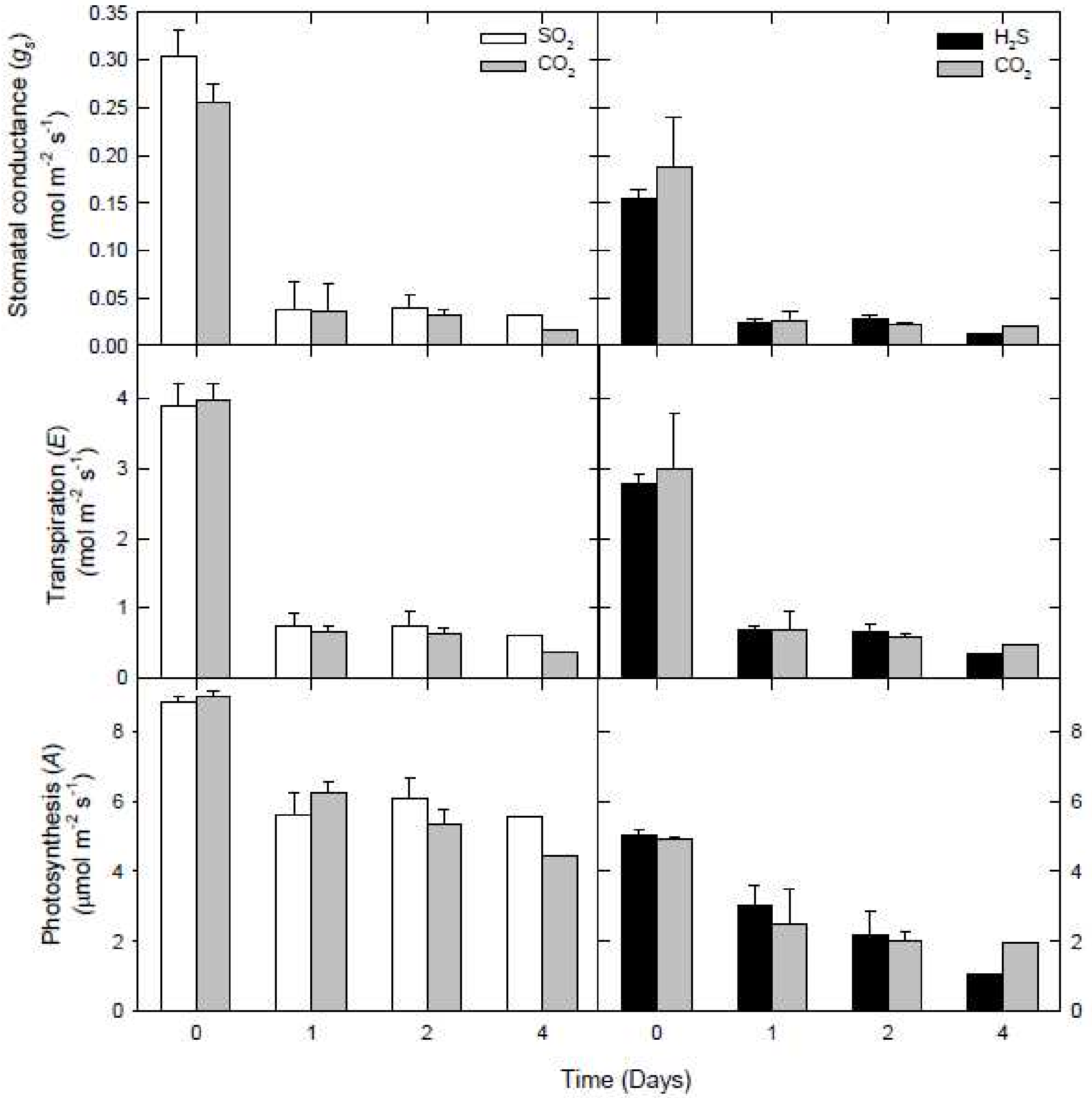
Stomatal conductance (g_s)
(mol m^{-2} s^{-1})
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
SO_2
CO_2
H_2S
CO_2
Transpiration (E)
(mol m^{-2} s^{-1})
4
3
2
1
0
Photosynthesis (A)
(µmol m^{-2} s^{-1})
8
6
4
2
0
0
1
2
4
0
1
2
4
Time (Days)

Figure 3

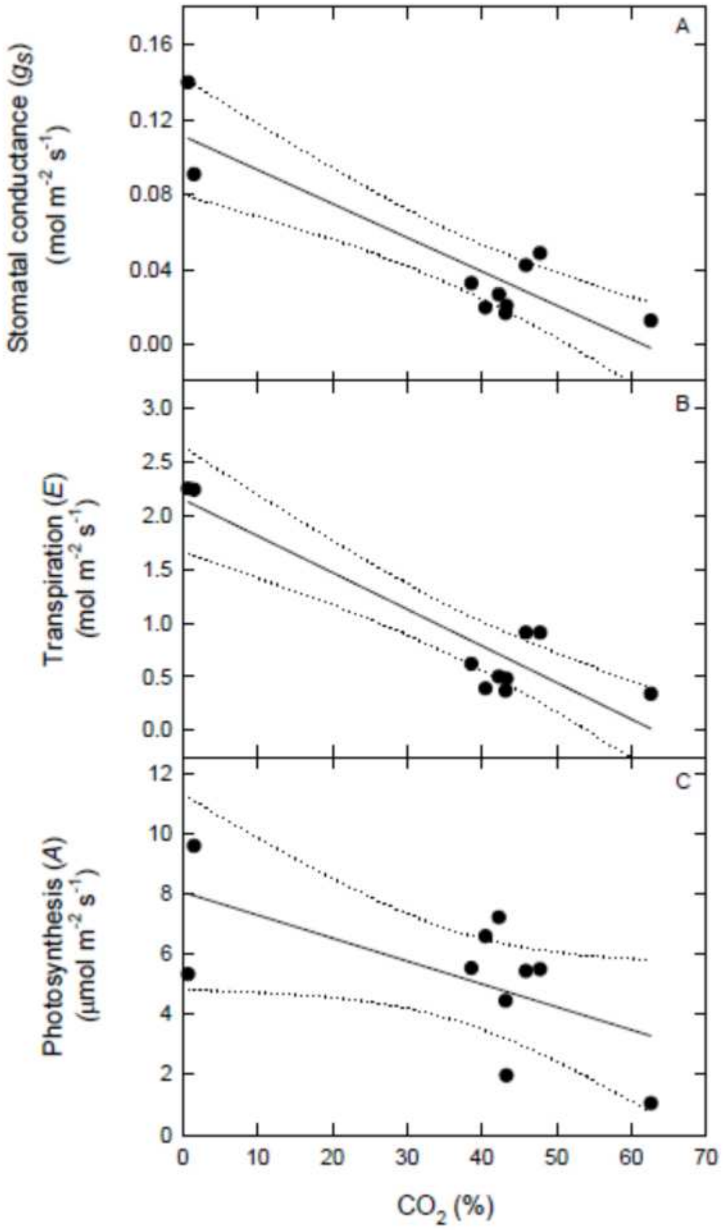
Stomatal conductance (g_S) (mol m^{-2} s^{-1})
0.16
0.12
0.08
0.04
0.00
A
Transpiration (E) (mol m^{-2} s^{-1})
3.0
2.5
2.0
1.5
1.0
0.5
0.0
B
Photosynthesis (A) (µmol m^{-2} s^{-1})
12
10
8
6
4
2
0
C
0
10
20
30
40
50
60
70
CO$_2$ (%)

Figure 4

336

Table 1. Range of concentrations of specific impurities (SO_2, H_2S) in the CO_2 gas stream from different capture technologies

	Oxy-fuel combustion			pre-combustion	post-combustion
	Raw/ dehumidified	double flashing	distillation		
CO_2 % v/v	74.8-85	95.8-96.7	99.3-99.4	95-99	99.6-99.8
SO_2 ppmv	50-100	0-4500	37-50	25	0-61.7
H_2S/COS ppmv				0-34000	

Adapted from Brown et al 2014; COS = carbonyl sulphide

Table 2. Mean gas concentrations measured as % CO_2 and % O_2 within the soil chambers.

Crop and impurity	**CO_2 concentration (%)**		**O_2 concentration (%)**	
	CO_2 gassed	CO_2 + impurity	CO_2 gassed	CO_2 + impurity
Wheat				
SO_2	42.3 (1.2)	40.5 (0.34)	11.0 (0.36)	12.1 (0.09)
H_2S	45.9 (2.08)	47.8 (5.83)	10.5 (0.30)	10.2 (0.38)
Beetroot				
SO_2	43.2 (2.54)	38.6 (3.93)	11.4 (0.48)	12.3 (2.48)
H_2S	43.3 (1.79)	62.6 (3.64)	11.3 (0.34)	7.3 (0.38)

[n = 3 for pure CO_2, 5 for CO_2 + impurity; (SEmean)]

Table 3. Percentage change in biomass and gas exchange parameters from CO_2-gassed control plants (black outline = H_2S effect, dashed outline = SO_2 effect). Data from the controls are actual values.

Crop and impurity	**Biomass**		**gas exchange parameters**		
	fresh weight (g)	dry weight (g)	photosynthetic rate (*A*)	stomatal conductance (g_s)	transpiration (E)
Wheat					
SO_2 added	+18.6	+6.25	-8.86	-25.19	-22.48
Control for SO_2 (CO_2 only)	2.57	0.42	7.217	0.027	0.503
H_2S added	-1.23	-11.25	+1.12	+16.1	+0.44
Control for H_2S (CO_2 only)	4.88	0.77	5.435	0.042	0.907
Beetroot					
SO_2 added	+6.08	+4.61	+24.12	+87.7	+66.8
Control for SO_2 (CO_2 only)	5.92	0.64	1.972	0.0215	0.476
H_2S added	-1.01	-6.81	-47.08	-35.39	-28.67
Control for H_2S (CO_2 only)	17.77	1.9	4.458	0.174	0.374

Table 4. Mean soil pH [n = 3 for CO_2 only, n = 5 for CO_2 + impurity, letters denote significant difference, see text].

Crop and impurity	**soil pH**		
	pre-gassed	CO_2 gassed	CO_2 + impurity
Wheat			
SO_2	5.23^{a}	5.61^{b}	5.45^{c}
H_2S	5.23^{a}	5.45^{b}	5.49^{b}
Beetroot			
SO_2	5.34^{a}	5.41^{b}	5.61^{b}
H_2S	5.34^{a}	5.63^{b}	5.61^{b}