

Article

Using Vegetation near CO₂ Mediated Enhanced Oil Recovery (CO₂-EOR) Activities for Monitoring Potential Emissions and Ecological Effects

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Academic Editor: Enrico Andreoli

Received: 30 October 2015 / Accepted: 14 December 2015 / xx Published: 2015

Abstract: CO₂ mediated enhanced oil recovery (CO₂-EOR) may lead to methods of CO₂ reduction in the atmosphere through carbon capture and storage (CCS); therefore, monitoring and verification methods are needed to ensure that CO₂-EOR and CCS activities are environmentally safe and effective. This study explored vegetation growth rate to determine potential ecological effects of emissions from CO₂-EOR activities. Plant relative growth rates (RGR) from plots within an oilfield and reference areas, before and after CO₂ breakthrough were used to assess CO₂-EOR activities impact surrounding vegetation. The trend for both areas was the decrease in RGR ratio during the study time; however, the decrease in RGR ratio was significantly less in the oilfield area compared to the reference area overall and by subcategories of pine, tree and shrub. Based on data from plant plots, RGR decreased in the reference and oilfield areas except one plot, which increased in RGR. Within the oilfield and reference areas, several species decreased significantly in RGR, but American olive increased in RGR. Vegetation monitoring could provide parameters related to the modeling potential effects of emissions on local ecosystems (species, groups and community) and serve as a necessary component to the monitoring and verification of CO₂-EOR and CCS projects. The challenge and limitations of vegetation monitoring were also discussed.

Keywords: enhanced oil recovery; CO₂ reduction; monitoring; verification

1. Introduction

One of the many considerations at the national and international levels is the maintenance of a steady supply of energy while being mindful of the potential environmental impact. Eighty-three percent of the USA fossil fuel energy consumption for 2010 was in the forms of petroleum (37%), natural gas (25%) and coal (21%) [1]. Oil fields can age over time and the expense of production rises to a point of unprofitability. After independent well pumping and field wide water flooding methods have been used, up to 75% of the original oil remains in place [2]. Innovative methods have to be developed for continuously supplying energy. Recent advances in enhanced oil recovery (EOR) methods have been used to produce oil previously considered cost prohibitive [3–5].

CO₂-mediated EOR (CO₂-EOR) is one type of EOR whereby supercritical CO₂ is injected into a depleting oil field to reduce viscosity and adherence properties of the crude, thereby reducing the energy required to move the crude towards a producing well [6]. In the oil industry, CO₂-EOR efforts have increased and as of 2010 there were 193 active CO₂-EOR projects in the USA [6]. Approximately 1.5 billion barrels (bbl) of oil have been recovered in the USA, using CO₂ injection with an estimated potential of recovering 47 bbl using current state of the art practices and an additional 30 bbl using future technologies [7]. CO₂-EOR recovery also provides an opportunity to study injected CO₂ within a reservoir that may in turn further develop CO₂ capture and storage technologies (CCS) as a means of reducing greenhouse gas emissions by storing CO₂ in geological reservoirs [8,9]. While CO₂-EOR increases oil returns and is a potential means of reducing greenhouse gas emissions through future geological storage of CO₂ [10], few studies have been conducted to understand the potential ecological effects of CO₂-EOR activities [11]. Concerns of CO₂-EOR include the formation of carbonic acid which may increase permeability allowing unwanted movement along faults [12] and the buoyant nature of CO₂ which has the potential to escape along improperly sealed wells or wells subjected to carbonic acid erosion [13,14]. The emitted CO₂ can greatly impact local ecosystems based on the magnitude and continuity. However, so far limited research has been conducted on the potential ecological effects of emissions for most CO₂-EOR and CCS activities because it might be considered as no effects to local ecosystems or not important for CO₂-EOR and CCS projects. Studies are needed to assess surrounding areas of CO₂-EOR to determine if CO₂-EOR affects local ecology. Such studies are also useful for long term monitoring strategies for geological storage of CO₂, such as carbon capture and storage technologies (CCS), which must be verified for obtaining greenhouse gas emission reduction credits [15] and must remain below ground for centuries to offset atmospheric gains of the past two centuries [16].

Increased atmospheric CO₂ can increase production of carbohydrates, which in turn increases in plant growth, so that with an increase in CO₂, plants generally respond with an increase in yield [17]. Plants may have a short-term response when exposed to elevated CO₂ [18] resulting in increased rates of photosynthesis and increased biomass accumulation [19]. Long-term exposure to CO₂ might result in accelerated growth. In forest systems, increased CO₂ concentrations can result in increased biomass, such as basal area increment, and the change of species composition (e.g., plants and animals) in the long term.

A CO₂-EOR pilot study at the Citronelle oilfield (Citronelle, AL, USA) presented an opportunity to explore the use of vegetation growth as a means of monitoring ecological impact of CO₂-mediated operations. The Citronelle oilfield, established in 1955, was unitized in 1966 and has had over 524 drilled

wells with about 400 currently active wells [20]. Thus such a monitoring technique may also be important with respect to verification as the same geological formation could be used in the future to store up to 2 billion tons of CO₂ from the nearby coal-fired electric generating plant [20]. The unknown behavior of injected CO₂ in a relatively small, defined area created a before and after injection scenario to assess whether the use of vegetation growth might be a viable monitoring strategy for CO₂-EOR activities and perhaps for storage verification as well. While the integrity of geological reservoir and wells in the area were assessed for CO₂ injection, potential emission of CO₂ demonstrated an opportunity to assess the ecological impact of an increase of CO₂ in the area. Because CO₂ can influence vegetation growth, monitoring adjacent vegetation that may be exposed to increased levels of CO₂ due to CO₂-EOR activities could serve as a means of recording excess CO₂ by increased growth rate. Given the amount of CO₂ injected (described below) our hypothesis was that CO₂-EOR activities would expose local vegetation to increased levels of CO₂ which in turn would have a higher growth rate than vegetation in areas not exposed to the produced CO₂. The objectives of this study were: (i) to examine the potential effects of CO₂-EOR activities on surrounding vegetation through direct measurement of plant growth rate; and (ii) to explore the implication of vegetation monitoring as a facet of CO₂-EOR and as a component of CCS monitoring and verification strategies.

2. Material and Methods

2.1. Study Description

This study was conducted as a cooperative agreement between federal, academic and private entities for the purpose of determining the feasibility of CO₂-EOR in the Citronelle oilfield and to extend oil production of the oilfield at large. Within the scope of this study tasks were set forth to establish a baseline to examine changes in types, populations and spatial distributions of vegetation in the landscape surrounding the injection site and to continue monitoring after CO₂ injection occurred [21].

The project was conducted within the Citronelle oilfield located in north Mobile County, Alabama of the USA. Within the oilfield the injection configuration consisted of an injection well (IW1) surrounded by four producing wells (PW1, PW2, PW3 and PW4) (Figure 1). Difficulties in converting well PW4 from plugged and abandoned (PNA) to a producing well proved unsuccessful and well PW5 was included in the configuration. The principle of establishing vegetation plots is to select sites with similar environmental condition (e.g., same soil type, plant communities and topography). Multiple vegetation plots and multiple plant species with many plant individuals should be used in order to minimize the impacts from other factors. Produced oil, water and gas from wells PW1, PW2 and PW3 were collected and separated at tank battery one (TB1); production from PW5 was collected and separated at tank battery two (TB2). CO₂ collected at the tank batteries were vented for the initial injection phase; however, future operations intend to collect and re-inject recaptured CO₂. For the first CO₂ injection phase a total of 8036 tons of supercritical CO₂ was injected into IW1 from November 2009–September 2010.

Breakthrough or first observed emission of injected CO₂ occurred on 25 May 2010 at production well PW5 then subsequently at production wells PW3 and PW2. Analysis of the emitted CO₂ indicated that the delta carbon-13 isotope ratio ($\delta^{13}\text{C}_{\text{CO}_2}$) was the same as the injected CO₂.

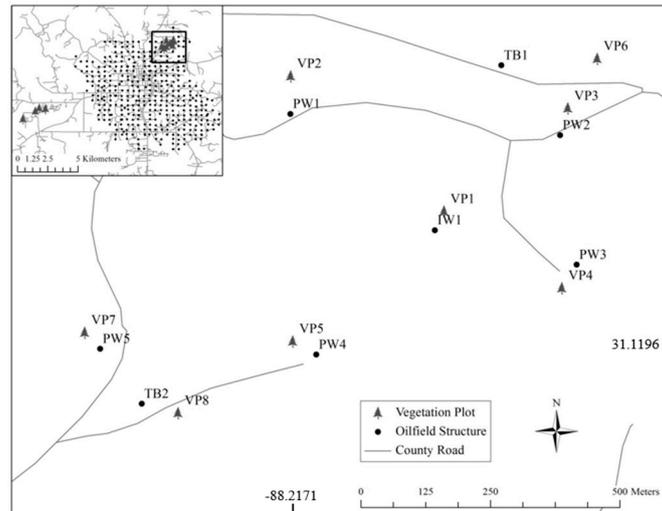


Figure 1. Relative location of vegetation plots adjacent to the injection configuration oilfield structures. The injection configuration includes the injection well (IW), production wells (PW) and associated tank batteries (TB). Insert indicates the position of the injection site and vegetation plots relative to the Citronelle oilfield.

2.2. *Vegetation Plots and Direct Measurement*

Based on the configuration of the CO₂ production site, vegetation plots (VP) were established within 200 m of the CO₂ injection well (IW1 (VP1)), each CO₂ production site well (PW1 (VP2), PW2 (VP3), PW3 (VP4a), PW4 (VP5) and PW5 (VP7)) and two associated tank batteries (TB1 (VP6) and TB2 (VP8)) for a total of 8 vegetation plots (Figure 1). Two reference plots were also established just north of the Citronelle oilfield. Due to land use change, both reference plots were destroyed within the first year and four new reference plots (GC1–GC4) were established southwest of the oilfield (Figure 2). This area was chosen to avoid conflict with private property owners and to ensure long term monitoring opportunities in an area unlikely to change in land use. Logging activity destroyed vegetation plot VP4a located at PW3 and plot VP4b was established at the same distance from PW3 to replace the original plot.

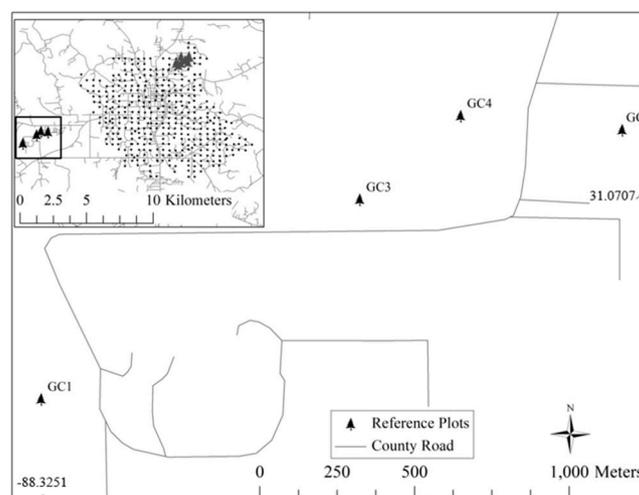


Figure 2. Relative location of reference plots located adjacent to a municipal golf course. Insert indicates the position of the vegetation plots relative to the Citronelle oilfield.

Each plot was 100 m² and within each plot the circumferences of all woody plants were measured at breast height for trees and at the base of the trunks before the first branch for underlying shrubs. Each plant was marked with paint for re-measurement and identified by plot and specimen number using aluminum tags. Plants were identified to genus or species if possible. Annual plot surveys ensured that tags remained in place and served as a means of recording annual growth. Circumference was used to calculate the basal area of each specimen. Plants not found when plots were re-measured were removed from analyses.

2.3. Data Analysis and Statistics

The relative growth rate was calculated from recorded basal area and standardized to growing months to reflect differences in dates of measurements. Monthly relative growth rate (RGR) was calculated using the formulas:

$$\text{RGR1} = ((Y2 - Y1)/Y1)/\text{GM} \quad (1)$$

$$\text{RGR2} = ((Y3 - Y1)/Y1)/2\text{GM} \quad (2)$$

where GM is defined as the total number of growing months between measurements, standardized to September. Due to the interference of logging, 2009 was used as the start year for all relative growth rate (RGR) comparisons. As such, Y1 was the basal area data collected in time period 2 (2009), Y2 was the basal area data collected in time period 3 (2010) and Y3 was the basal area data collected in time period 4 (2011) (Table 1). The results of RGR1 and RGR2 were used to examine relative growth rate in relation to Y1 for 2009 to 2010 and for 2010 to 2011 in the oilfield and reference areas:

$$\text{RGR ratio} = \text{RGR2}/\text{RGR1} \quad (3)$$

Table 1. Months between re-measurements of plots from the previous year.

Plot	2009	2010	2011
VP2	14	12	12
VP3	15	12	12
VP4b	-	9	12
VP5	15	12	12
VP6	15	12	12
VP7	12	12	12
VP8	12	12	12
GC1	-	6	12
GC2	-	6	12
GC3	-	6	12
GC4	-	6	12

An independent-samples *t*-test was conducted to compare the mean RGR ratio of plots in the oilfield to the mean RGR ratio of plots in the reference area. This comparison was also made for subcategories of trees, shrubs, hardwoods and pine. Assumptions of equal variance between oilfield and reference plots were tested with Levene's test for equality of variances [22]. RGR ratios of subgroups were also compared, these included vegetation sorted by hardwood or pine and trees or shrub.

3. Results

Species composition for the oil field and reference area by plot is listed in Table 2. Conifers were present in each area, however, planted loblolly occurred in the oilfield area and longleaf pine occurred in the reference area. The dominant shrubs were Carolina holly and yaupon holly; both species were present in each area.

Table 2. Species and number by plot for both the impact (VP2–8) and reference area (GC1–4).

Common Name	Latin Name	VP2	VP3	VP4b	VP5	VP6	VP7	VP8	GC1	GC2	GC3	GC4
Swamp maple	<i>Acer rubrum</i> spp.				4							
Beech	<i>American Fagus grandifolia</i>				3							
Pawpaw	<i>Asimina triloba</i>				3							2
Mockernut	<i>Carya tomentosa</i> (Poir.) Nutt.			6							5	1
Dogwood	<i>Cornus florida</i>				5							2
Leatherwood	<i>Cyrilla racemiflora</i>			63								
Persimmon	<i>Diospyros virginiana</i>	13	3				8	5				
Huckleberry	<i>Gaylussacia frondosa</i>				5		1	2	1	1		4
Carolina holly	<i>Ilex ambigua</i>	34	2					2		25	26	28
Holly sp.	<i>Ilex</i> sp.											12
Winterberry holly	<i>Ilex verticillata</i>			2								
Yaupon holly	<i>Ilex vomitoria</i>	11	28		21	49	9	2		12	45	11
Eastern Redcedar	<i>Juniperus virginiana</i> L.											1
Poplar	<i>Liriodendron tulipifera</i> L.				9							
Magnolia	<i>Magnolia grandiflora</i> L.				1							
Sweetbay	<i>Magnolia virginiana</i>				4							
Blackgum	<i>Nyssa sylvatica</i>											
American olive	<i>Osmanthus americanus</i>				3	2						15
Long leaf pine	<i>Pinus palustris</i> Mill.								85	30	4	12
Loblolly pine	<i>Pinus taeda</i> L.	20	21			30	20	9				
Plum	<i>Prunus americana</i> Marsh.								1			
White oak	<i>Quercus alba</i> L.							1			2	3
Turkey oak	<i>Quercus laevis</i>	7						15				
Laurel oak	<i>Quercus laurifolia</i>	6				1		3				
Overcup oak	<i>Quercus lyrata</i> Walt.	1									1	
Blackjack oak	<i>Quercus marilandica</i>	2										
Water oak	<i>Quercus nigra</i> L.	1								2	4	1
Willow oak	<i>Quercus phellos</i> L.				1	2						
Black oak	<i>Quercus velutina</i> Lam.					1					4	1
Sassafras	<i>Sassafras albidum</i> (Nutt.)						13					
Elm sp	<i>Ulmus</i> sp.											1
Quercus spp.		9	2	6			2			1	3	
Total		104	56	77	59	85	53	39	87	71	109	79

3.1. Comparison of Relative Growth Rate Ratio before and after Breakthrough (*t*-Test)

There was a significant difference in the RGR ratio between vegetation plots located in the reference area (average: $\bar{x} = 0.96$, standard deviation: $SD = 0.12$) and all oilfield area ($\bar{x} = 0.66$, $SD = 0.10$); $t(9) = 4.013$, $p = 0.003$ (Figure 3). There was a significant difference in all subgroups used to examine RGR ratio with the exception of hardwoods. Hardwood RGR ratio in the reference area ($\bar{x} = 0.71$, $SD = 0.09$) and all oilfield area ($\bar{x} = 0.60$, $SD = 0.16$); $t(9) = -1.16$, $p = 0.276$. Pine RGR ratio in the reference area ($\bar{x} = 0.65$, $SD = 0.10$) was significantly different than the RGR ratio in the oilfield area ($\bar{x} = 1.09$, $SD = 0.13$); $t(7) = 5.446$, $p = 0.001$. The RGR ratio for the subcategory of trees in the reference area ($\bar{x} = 0.67$, $SD = 0.11$) was significantly different than the RGR ratio in the oilfield area ($\bar{x} = 0.97$, $SD = 0.13$); $t(9) = 3.903$, $p = 0.004$. The RGR ratio for the subcategory of shrubs in the reference area ($\bar{x} = 0.62$, $SD = 0.05$) was significantly different than the RGR ratio in the oilfield area ($\bar{x} = 1.02$, $SD = 0.28$); $t(5.5) = 3.396$, $p = 0.017$.

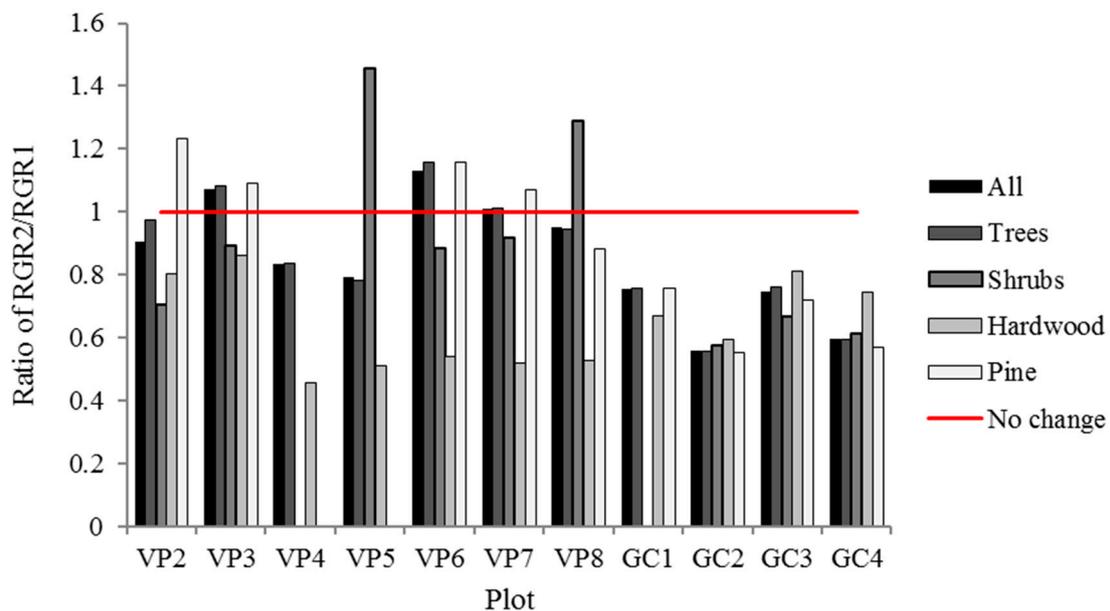


Figure 3. Overall ratio of relative growth rate (RGR) for the oilfield and reference area and by subcategories of hardwoods, pines, trees and shrubs. Line indicates no change in relative growth rate.

3.2. Oilfield Area (RM-ANOVA)

The overall trend in monthly RGR for the oilfield area was a decrease over time with the exception of plot VP5 (Figure 3). The results of repeated measures ANOVA (RM-ANOVA) analyses indicated a significant change in monthly RGR over the course of the study for all vegetation within the oilfield ($p < 0.0005$) (Table 3). *Post hoc* comparisons using Bonferroni correction indicated an overall significant decrease in monthly RGR between 2008–2009 and 2009–2010 ($p < 0.0005$), between 2009–2010 and 2010–2011 ($p = 0.05$) and between 2008–2009 and 2010–2011 ($p < 0.0005$) (Table 3).

Table 3. Results of repeated measures ANOVA for overall monthly growth rate (RGR) and monthly RGR by plots.

Group	F Statistic, p Value	2008–2009, 2009–2010		2009–2010, 2010–2011		2008–2009, 2010–2011	
		$\bar{x} \pm SD$	p Value	$\bar{x} \pm SD$	p Value	$\bar{x} \pm SD$	p Value
Oilfield	$F(1.9, 850.7) = 23.34$, $p \leq 0.0005$ *	0.58 ± 0.54 , 0.44 ± 0.45	<0.0005 *	0.44 ± 0.45 , 0.38 ± 0.40	0.050 *	0.58 ± 0.54 , 0.38 ± 0.40	<0.0005 *
VP1	$F(2, 94) = 9.12$, $p \leq 0.0005$ *	0.15 ± 0.22 , 0.24 ± 0.33	0.388	0.24 ± 0.33 , 0.44 ± 0.45	0.034 *	0.15 ± 0.22 , 0.44 ± 0.45	<0.0005 *
VP2	$F(2, 206) = 19.09$, $p < 0.0005$ *	0.63 ± 0.49 , 0.45 ± 0.42	0.019 *	0.45 ± 0.42 , 0.27 ± 0.32	0.017 *	0.63 ± 0.49 , 0.27 ± 0.32	<0.0005 *
VP3	$F(2, 110) = 5.38$, $p = 0.006$ *	0.89 ± 0.67 , 0.67 ± 0.57	0.228	0.67 ± 0.57 , 0.54 ± 0.41	0.389	0.89 ± 0.67 , 0.54 ± 0.41	0.009 *
VP5	$F(1.8, 109.2) = 1.57$, $p = 0.212$	0.17 ± 0.23 , 0.24 ± 0.29	0.225	0.24 ± 0.29 , 0.25 ± 0.36	1.000	0.17 ± 0.23 , 0.25 ± 0.36	0.379
VP6	$F(1.8, 149.5) = 14.10$, $p \leq 0.0005$ *	0.90 ± 0.60 , 0.55 ± 0.50	0.001 *	0.55 ± 0.50 , 0.46 ± 0.47	0.547	0.90 ± 0.60 , 0.46 ± 0.47	<0.0005 *
VP7	$F(2, 104) = 3.72$, $p = 0.028$ *	0.66 ± 0.41 , 0.47 ± 0.49	0.139	0.47 ± 0.49 , 0.46 ± 0.45	1.000	0.66 ± 0.41 , 0.46 ± 0.45	0.061
VP8	$F(2, 76) = 5.17$, $p = 0.008$ *	0.72 ± 0.62 , 0.48 ± 0.40	0.227	0.48 ± 0.40 , 0.36 ± 0.30	0.464	0.72 ± 0.62 , 0.36 ± 0.30	0.015 *

* means statistically significant at $p < 0.05$ level.

By plot, there was a significant decrease in monthly RGR over time (VP2 ($p < 0.0005$), VP3 ($p = 0.006$), VP6 ($p < 0.0005$), VP7 ($p = 0.028$) and VP8 ($p = 0.008$)) with the exception of plot VP5. *Post hoc* analysis indicated a significant decrease in monthly RGR between 2008–2009 and 2009–2010 for plots VP2 ($p = 0.019$) and VP6 ($p = 0.001$) and a less than significant decrease in monthly RGR for plots VP3, VP7 and VP8. Plot VP5 increased, although not significantly. Between 2009–2010 and 2010–2011 there was a significant decrease in monthly RGR in plot VP2 ($p = 0.017$) and plots (VP3, VP6–VP8) decreased in in monthly RGR but not at a significant level. Plot VP5 showed a slight but non-significant increase in monthly RGR. Comparison between 2008–2009 and 2010–2011 indicated a significant decrease in monthly RGR plots VP2 ($p < 0.0005$), VP3 ($p = 0.009$), VP6 ($p < 0.0005$) and VP8 ($p = 0.15$). The decrease in monthly RGR in plot VP7 was not significant and there was an increase in monthly RGR in plot VP5, although not significant.

3.3. Reference (Paired *t*-Tests)

There was a general trend to decrease in monthly RGR in the reference area (Figure 3). The results of a paired *t*-test indicated a statistically significant decrease in monthly RGR for all vegetation between years 2009–2010 and 2010–2011 ($p < 0.0005$) (Table 4). By plot, there was a significant decrease in monthly RGR between 2009–2010 and 2010–2011 for plot GC1 ($p = 0.002$), GC2 ($p < 0.0005$) and GC4 ($p = 0.026$). Monthly RGR for GC3 also decreased; however, the result was not statistically significant.

3.4. VP4b (Paired *t*-Tests)

Due to logging activity oilfield plot VP4b was not measured enough times to use the same RM ANOVA analyses as used on the other oil field plots and was instead analyzed using paired *t*-tests. The trend in monthly RGR can be found in Figure 3. Overall, there was a significant decrease ($p = 0.003$) in monthly RGR between 2009–2010 and 2010–2011 in plot VP4b (Table 4).

Table 4. Results of paired *t*-tests of overall monthly RGR and monthly RGR by plots. Results for plot VP4b are included.

Reference	2009–2010 $\bar{x}(T2) \pm SD$	2010–2011 $\bar{x}(T3) \pm SD$	<i>t</i> Statistic	<i>p</i> Value
Total veg	0.57 ± 0.63	0.41 ± 0.46	$t(349) = 4.605$	<0.0005 *
GC1	0.99 ± 0.58	0.72 ± 0.37	$t(85) = 3.247$	0.002 *
GC2	0.45 ± 0.49	0.22 ± 0.35	$t(72) = 4.286$	<0.0005 *
GC3	0.51 ± 0.67	0.46 ± 0.49	$t(111) = 0.715$	0.476
GC4	0.38 ± 0.62	0.24 ± 0.46	$t(78) = 2.266$	0.026 *
Impact-VP4	0.78 ± 0.52	0.56 ± 0.45	$t(78) = 3.017$	0.003 *

* means statistically significant at $P < 0.05$ level.

3.5. Hardwood Trees

Hardwoods in the oilfield area showed a general trend to decrease in monthly RGR with the exception of plot VP5 (Figure 3). Results of a RM-ANOVA indicated a significant difference in monthly RGR for all hardwood within the oilfield area ($p < 0.0005$) and a *post hoc* Bonferroni correction indicated a significant decrease in monthly RGR between 2008–2009 and 2009–2010 ($p = 0.015$), between 2009–2010 and 2010–2011 ($p < 0.0005$) and between 2008–2009 and 2010–2011 ($p < 0.0005$) (Figure 3). Between 2008–2009 and 2009–2010 plots VP2, VP3, and VP6–VP8 decreased in monthly RGR but not at a level of significance. Plot VP5 showed an increase in monthly RGR but this increase was not significant. Comparison of monthly RGR between 2009–2010 and 2010–2011 resulted in a decrease in all oilfield plots except for VP5; however, the decrease was significant only in plot VP2 ($p = 0.001$). Plot VP5 showed an increase in monthly RGR. A comparison between 2008–2009 and 2010–2011 showed a decrease in all oilfield plots except VP5, which increased. Plots VP2 ($p = 0.002$), VP6 ($p = 0.001$) and VP8 ($p = 0.002$) decreased significantly in monthly RGR. Plot VP5 showed an increase in RGR but not at the level of significance.

Hardwoods in the reference area showed an overall decrease in monthly RGR (Figure 3). Paired *t*-tests indicated an overall significant decrease in monthly RGR in hardwoods from 2009–2010 to 2010–2011 ($p = 0.007$). All reference plots decreased in monthly RGR over time and the decrease in plot GC2 was statistically significant ($p = 0.006$).

3.6. Coniferous Trees

Conifers in the oilfield area showed an overall decrease in monthly RGR (Figure 3). Results of an RM-ANOVA indicated a significant change in monthly RGR for all conifers within the oilfield ($p < 0.0005$) and a *post hoc* Bonferroni correction indicated a significant decrease in monthly RGR between 2008–2009

and 2009–2010 ($p < 0.0005$) and between 2008–2009 and 2010–2011 ($p < 0.0005$). There was a significant change in monthly RGR in all oilfield plots with conifers, VP2 ($p < 0.0005$), VP3 ($p = 0.006$), VP6 ($p < 0.0005$), VP7 ($p = 0.009$) and VP8 ($p = 0.002$). *Post hoc* results indicated a decrease in monthly RGR in all plots comparing 2008–2009 and 2009–2010, plots VP2 ($p < 0.0005$), VP3 ($p = 0.013$), VP6 ($p < 0.0005$) and VP7 ($p = 0.038$) were significant. The monthly RGR between 2009–2010 and 2010–2011 increased in all plots except VP8, which decreased. None of the changes were statistically significant. The monthly RGR between 2008–2009 and 2010–2011 decreased significantly overall in plots VP2 ($p = 0.002$), VP6 ($p = 0.001$) and VP8 ($p = 0.015$). Plots VP3 and VP7 also decreased in monthly RGR but not significantly.

Conifers in the reference area showed an overall decrease in monthly RGR (Figure 3). Paired *t*-tests results indicated a significant decrease in all reference conifers between 2009–2010 and 2010–2011 ($p < 0.0005$). By plot, there was no change in monthly RGR in reference plot GC3 and the remaining plots decreased in monthly RGR but only plots GC1 ($p = 0.003$) and GC2 ($p = 0.001$) were significant.

3.7. Trees

In the oilfield there was an overall decrease in monthly RGR in the tree subcategory (Figure 4). Results of a RM-ANOVA indicated a significant change in monthly RGR for all trees within the oilfield ($p < 0.0005$) and a *post hoc* Bonferroni correction indicated a significant decrease in monthly RGR between 2008–2009 and 2009–2010 ($p < 0.0005$) and between 2008–2009 and 2011–2011 ($p < 0.0005$). By plot, there was a significant change in monthly RGR in VP2 ($p < 0.0005$), VP5 ($p = 0.043$), VP6 ($p = 0.008$), VP7 ($p = 0.005$) and VP8 ($p = 0.006$). Between 2008–2009 and 2009–2010 the monthly RGR decreased in all plots except VP5. Plots VP2, ($p = 0.001$), VP6 ($p < 0.015$) and VP7 ($p = 0.041$) decreased significantly. Between 2009–2010 and 2010–2011 no plots changed significantly. A comparison of 2008–2009 and 2010–2011 showed a significant decrease in VP2 ($p < 0.0005$), VP7 ($p = 0.008$) and VP8 ($p = 0.002$). All others either did not change (VP5) or decreased but without significance (VP3, VP5 and VP6).



Figure 4. Relative growth rate of oilfield and reference areas and by plots therein. Includes a comparison of hardwoods and conifers by oilfield and reference areas and plots within.

Trees in the reference area generally decreased in monthly RGR (Figure 4). Paired *t*-test results indicated an overall significant decrease in monthly RGR of trees ($p < 0.0005$). By plot, there was a significant decrease between 2009–2010 and 2010–2011 in GC1 ($p = 0.002$) and GC2 ($p = 0.003$). The remaining plots decreased but without significance.

3.8. Shrubs

Shrubs decreased in monthly RGR in the oilfield area (Figure 4). Results of an RM-ANOVA indicated a significant difference in monthly RGR for all shrubs within the oilfield ($p < 0.0005$) and a *post hoc* Bonferroni correction indicated a significant decrease in monthly RGR from 2008–2009 to 2010–2011 ($p < 0.014$), from 2009–2010 to 2010–2011 ($p = 0.007$) and from 2008–2009 to 2010–2011 ($p < 0.0005$). By plot, VP2 ($p < 0.0005$), VP3 ($p = 0.006$) and VP6 ($p < 0.0005$) were significant. From 2008–2009 to 2010–2011, with the exception of VP5 which increased, all plots decreased in monthly RGR between 2008–2009 and 2009–2010, however, only plot VP6 ($p = 0.005$) was significant. Between 2009–2010 and 2010–2011 all plots decreased in monthly RGR with the exception of plot VP5, which increased in monthly RGR. Only VP2 ($p = 0.002$) was significant. From 2008–2009 to 2010–2011 all plots decreased in monthly RGR except for plot VP5, only plots VP2 ($p < 0.0005$), VP3 ($p = 0.011$) and VP6 ($p < 0.0005$) were significant.

Shrubs in the reference area generally declined in RGR in the reference area (Figure 4). Based on paired *t*-tests there was an overall significant decrease in monthly RGR of shrubs between 2009–2010 and 2010–2011 ($p = 0.008$). All plots showed a decrease in monthly RGR, however, only the decrease in plot GC2 was significant ($p = 0.004$).

3.9. Species Level

At the oil well field, with the exception of American olive, most species decreased in monthly RGR over time (Figure 5). American olive ($p = 0.028$), Carolina holly ($p = 0.006$), laurel oak ($p = 0.048$) and poplar ($p = 0.028$), turkey oak ($p = 0.002$) and yaupon holly ($p < 0.0005$) were significantly different overall, and Bonferroni *post hoc* analysis indicated a significant decrease in turkey oak ($p = 0.047$) and yaupon holly ($p = 0.020$) between 2008–2009 and 2009–2010, in Carolina holly ($p = 0.043$) between 2009–2010 and 2010–2011 and when comparing 2008–2009 and 2010–2011, there was a significant decrease in monthly RGR for C. holly ($p = 0.013$), turkey oak ($p = 0.002$) and yaupon holly ($p < 0.0005$).

In the reference area all species decreased in monthly RGR (Figure 6). Only Carolina holly ($p = 0.011$), leatherwood ($p = 0.006$), and long leaf pine ($p < 0.005$) decreased significantly in monthly RGR.

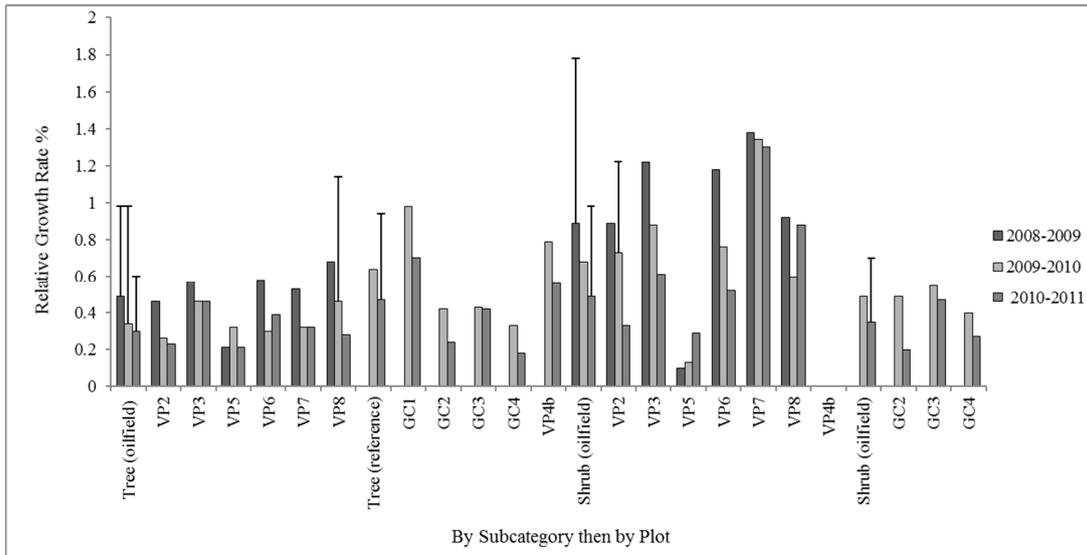


Figure 5. Relative growth rate of trees and shrubs subcategories with plots if the numbers where n was ten or greater.

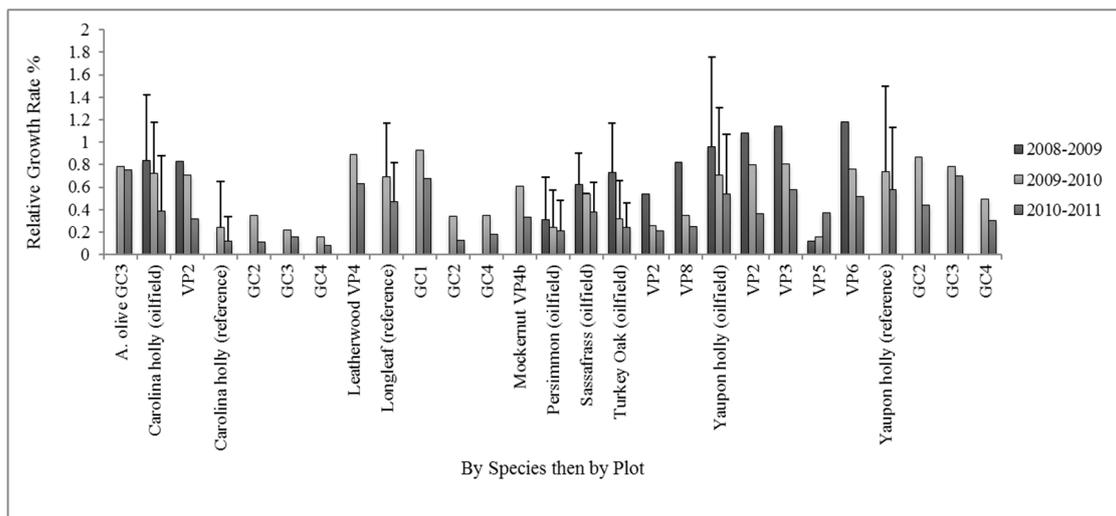


Figure 6. Relative growth rate of some species at oilfield and reference areas where n was ten or greater.

4. Discussion

In this study, we examined the potential use of vegetation monitoring as one of the strategies to determine local ecological effects of CO₂-EOR. The overall comparison of reference plots to oilfield plots prior to and post CO₂ breakthrough was not statistically significant. However, at the plot level, the general trend was the decrease in monthly RGR over time for both the reference and oilfield areas and in every subcategory considered for both oilfield and reference areas. The exception to this trend was plot VP5 and although VP5 lacked statistical significance, this does not eliminate biological significance as the general trend in RGR was to decrease. In addition, there was a significant difference in RGR ratio for plots and species groups between oilfield and reference site. Since the predicted influence of CO₂ is an increase in growth when the increase in level is moderate, the increase in monthly RGR for plot VP5

is an interesting find. Thus, when considering spatial and temporal scales, it appears that there was a general decrease in monthly RGR at a spatial scale that included both the reference and oilfield area with the exception of plot VP5. Within the injection configuration the order of CO₂ breakthrough was PW5, PW3 and PW2 [23]. The location of breakthrough occurrences suggested that the movement of injected CO₂ was influenced by a geological feature, the direction of the maximum horizontal compressive stress in the southeast of the USA, which occurred in the N60°E to N80°E direction [23]. The observation of an additional well that subsequently demonstrated breakthrough some distance SW of the injection configuration further supported this hypothesis. The location of plot VP5 occurs along a line of the same direction between PW2 and PW3 to the NE and PW4 and PW5 to the SW (Figure 1). Moreover, soil gas studies at PW1–PW5 and IW1 indicated an increase in soil CO₂ flux at PW2 in August 2010 (post breakthrough) compared to a previous measurement in August 2008 [23]. Elevation is not uniform throughout the area and VP5 is located in an area that is lower in elevation than the CO₂ injection well, TB1, PW2 and PW3, the CO₂ tank battery and production wells that have produced injected CO₂. It is possible that if excess CO₂ were present and temperatures were cooler, CO₂, which is denser than air, could sink to this lower lying area and increase available concentrations of CO₂ so that this area would be more likely to receive increased CO₂ exposure. Even when winds increased it was possible for CO₂ to linger in the relatively topographical depressions [24]. Plot VP1, the vegetation plot that also occurs in between the productions wells marked by breakthrough, was also increasing in monthly RGR, however, the effects of logging cannot be separated and are thus not considered. The regional weather would also affect vegetation growth, but its influence would be similar across different vegetation plots, such as decrease in RGR. The growth deviating from the general trend would be the impact from CO₂-EOR. That's the importance for establishing many vegetation plots.

Our study is the first to monitor the potential effects of the confirmed emissions from CO₂-EOR. Thus far, no conventional approaches have been developed to do this kind of evaluation because it is usually assumed that there is no emissions from CO₂-EOR or not important for CO₂-EOR projects. Cost prohibitive, controlled studies of the impacts of artificially increased CO₂ have been conducted through free air CO₂ enrichment (FACE) experiment, however, unlike the FACE experiments where all the vegetation is uniformly exposed to CO₂, plots in the oilfield are more likely to be exposed to released CO₂ than the reference area but the direction and magnitude were unknown. Since CO₂ would greatly increase plant growth, had all plots demonstrated an increase in RGR, this would have suggested an effect at a different scale than the observed oilfield or no effect. Vegetation plots around the different directions of the CO₂-EOR project site and reference site were necessary in this study.

One of the difficulties of monitoring the release of injected CO₂ is that there are many potential ways in which CO₂ could escape such as through a geologically faulted area or through previously established wells [8]. When establishing a monitoring regime for CO₂-mediated EOR sites or for carbon sequestration activities, the potential escape locations may be unknown thus established vegetation plots may not be influenced by emissions. This is also influenced by the scale of monitoring. Clearly defining of an area of potential CO₂ seepage is the first step. Although thoroughly considered a priori, the actual movement of injected CO₂ may not be known until after injection. In this study breakthrough results from monitored injection wells could suggest a more defined area for future long term monitoring of ecological effects of CO₂-EOR activity as the injected CO₂ appeared to have followed an underlying geological feature.

Assessment of vegetation, especially using a direct measurement of basal areas at plots and further investigation of monthly RGR suggests a site specific strategy to detect and monitor vegetation adjacent to CO₂-EOR activities at a small spatial and temporal scale and may be well complimented by larger scale indirect methods such as Normalized Difference Vegetation Index (NDVI) studies depending on the area of interest and the scale of CO₂-EOR activities. In this case, with the probable location of escape more narrowly defined, smaller scale approaches might then become more feasible with respect to cost, e.g., soil gas monitoring and $\delta^{13}\text{C}$ CO₂ analysis at trophic levels. The timescale for vegetation response will depend on the purposes of monitoring, time period of EOR, condition of oil wells and also funding resource availability. The vegetation monitoring should start before the EOR project in order to create background information and last several years after the end of EOR project. It would be better to have monitoring in different time scales, such as month, year or decade. Due to the limited funding support, our monitoring work completed at the end of EOR project in this research. The other notable disadvantage to using vegetation monitoring is the potential for data loss due to natural disturbances or wildlife movement. Careful consideration to plot establishment is necessary.

Assessment of the potential impacts of CO₂-EOR activities on local vegetation may serve as a means of complimenting methods used to monitor injected CO₂ within the geological reservoir, along with effects on hydrology, soil concentrations and surrounding atmospheric gas levels [25]. With the integration of information from other forms of monitoring more quantified verification and modeling is possible. Because trees are long-lived from an ecological perspective, vegetation monitoring across decades is a possible indicator for impacts of CO₂-EOR activities through changes in growth or through a decline in vegetation health. The benefit of establishing vegetation plots prior to CO₂-EOR activity is that vegetation may be monitored for years to come using both direct and indirect techniques. If the same geological reservoir is used for CCS activities, a baseline established prior to injection can be used for decades to examine the impact and perhaps verify retention of geologically stored CO₂.

5. Conclusions

By comparing the monthly RGR of vegetation plots located in an area used for CO₂-EOR and vegetation plots located in a reference area, we observed that one vegetation plot located in the oil field area increased in monthly RGR where remaining plots were generally categorized by decreased monthly RGR across the study period and also some plant species were sensitive to change. These results suggest that vegetation monitoring could be used as a component of a larger monitoring and verification program for CO₂-mediated EOR and carbon capture and sequestration. The value of vegetation monitoring approach includes (i) directly providing evidence of change in plant growth; (ii) identifying the sensitive plants; (iii) providing parameters for future modeling the potential ecological effects from CO₂-EOR to local ecosystems; and (iv) forming strategy for future integrated monitoring system for CO₂-EOR and CCS projects. Despite vegetation growth could be affected by many factors including the uncertainty of CO₂ emission (e.g., direction and quantity), careful consideration of the location of plots, selection of species, assessment of community maturity, desired time scale of interest and the access to local meteorological, soil and topographical variables will strengthen inferences that may be drawn from vegetation monitoring of CO₂-EOR activities. Moreover, used in conjunction with typical monitoring strategies of CO₂-EOR activities such as injection and formation pressure, soil gas monitoring, geochemical and geophysical monitoring, and

air quality monitoring, vegetation monitoring may serve as a means of quantifying and modeling the ecological effects of CO₂-EOR activities as well as a means of storage verification. More intensive research should be conducted on vegetation monitoring and modeling on EOR and carbon storage projects.

Acknowledgments

This study was partially supported by DOE/NETL Cooperative Agreement Number DE-FC26-06NT43029, ALEPSCoR and USDA National Institute of Food and Agriculture McIntire Stennis project (1008643). Our sincerest thanks to our invaluable colleagues at Alabama A & M University: Dawn Lemke, Clint Patterson and Dana Virone. We are grateful for the assistance from volunteers Jeremy Breaux, Sarah Breaux, Jane Roberts, Jeff Roberts and Walter Nelson. Al Schotz at Auburn University provided additional assistance with tree identification.

Author Contributions

Both Xiongwen Chen and Kathleen A. Roberts contributed in experimental design; field measurements; data analysis; and manuscript writing.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. EIA (Energy Information Administration). AEO 2012 Early Release Overview. Available online: http://205.254.135.7/forecasts/aeo/er/early_fuel.cfm (accessed on 26 October 2015).
2. Wildenborg, A.F.B.; van der Meer, L.G.H. The use of oil, gas and coal fields as CO₂ sinks. In Proceedings of the IPCC Workshop on Carbon Dioxide Capture and Storage. 18–21 November 2002, Regina, Canada; ECN: Petten, The Netherlands.
3. Babadagli, T. Development of mature oil fields—A review. *J. Petrol. Sci. Eng.* **2007**, *57*, 221–246.
4. Zhang, X.; Xiang, T. Review on microbial enhanced oil recovery technology and development in China. *Int. J. Petr. Sci. Tech.* **2010**, *4*, 61–80.
5. Giacchetta, G.; Leporini, M.; Marchetti, B. Economic and environmental analysis of a Steam Assisted Gravity Drainage (SAGD) facility for oil recovery from Canadian oil sands. *Appl. Energy.* **2015**, *142*, 1–9.
6. Hyne, H.J. *Nontechnical guide to petroleum geology, exploration, drilling, and production*; Tulsa, PennWell Corporation: Nashua, NH, USA, **2001**; pp. 1–598.
7. Moritis, G. Special report: EOR/Heavy Oil Survey: CO₂ miscible, steam dominate enhanced oil recovery processes. *Oil Gas J.* **2010**, *14*, 36–53.
8. Benson, S.; Cook, P.; Anderson, J.; Bachu, S.; Nimir, H.B.; Basu, B.; Bradshaw, J.; Deguchi, G.; Gale, J.; von Goerne, G.; *et al.* Underground geological storage. In *IPCC Special Report on Carbon Dioxide Capture and Storage*; Metz, B., Davidson, O., de Coninck, H.C., Loos, M., Meyer, L., Eds.; Cambridge University Press: Cambridge, UK, **2005**; pp. 196–276.

9. Rubin, E.; Meyer, L.; de Coninck, H. Technical summary. In *IPCC Special Report on Carbon Dioxide Capture and Storage*. Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L., Eds.; Cambridge University Press: Cambridge, UK, **2005**; pp. 17–50.
10. ARI. US Oil Production Potential from Accelerated Deployment of Carbon Capture and Storage. Advanced Resources International, Inc, Arlington, VA, USA. **2010**, White paper.
11. Leuning, R.; Etheridge, D.; Luhr, A.; Dunse, B. Atmospheric monitoring and verification technologies for CO₂ geosequestration. *Int. J. Greenh. Gas Con.* **2008**, *2*, 401–414.
12. Pruess, K. On leakage from geologic storage reservoirs of CO₂. In *Proceedings of CO₂SC Symposium 2006*; Lawrence Berkeley National Laboratory, Berkeley, California, 20–22 March 2006.
13. Damen, K.; Faaij, A.; Turkenburg, W. Health safety and environmental risks of underground CO₂ storage—Overview of mechanisms and current knowledge. *Climatic Change* **2006**, *74*, 289–297.
14. Zhang, M.; Bachu, S. Review of integrity of existing wells in relation to CO₂ geological storage. What do we know? *Int. J. Greenh. Gas Con.* **2010**, *5*, 826–840.
15. Dooley, J.J.; Dahowski, R.T.; Davidson, C.L. CO₂ driven Enhanced Oil Recovery as A Stepping Stone to What? Report PNNL–19557, Pacific Northwest National Laboratory, Richland, WA, USA, **2010**.
16. NETL (National Energy Technology Laboratory). Monitoring, verification, and accounting of CO₂ stored in deep geologic formations. **2009**. Available online: www.netl.doe.gov/technologies/carbon_seq/refshelf/MVA_Document.pdf (accessed on 26 October 2015).
17. Kimball, B.A.; Mauney, J.R.; Nakayama, F.S.; Idso, S.B. Effects of increasing atmospheric carbon dioxide on vegetation. *Vegetation* **1993**, *104–105*, 65–75.
18. Moore, B.D.; Cheng, S.H.; Sims, D.; Seeman, J.R. The biochemical and molecular basis for photosynthetic acclimation to elevated atmospheric CO₂. *Plant Cell Environ.* **1999**, *22*, 567–582.
19. Pritchard, S.G.; Rodgers, H.; Prior, S.A.; Peterson, C.M. Elevated CO₂ and plant structure: a review. *Global Change Biol.* **1999**, *5*, 807–837.
20. Esposito, R.A.; Pashin, J.C.; Walsh, P.M. Citronelle Dome: A giant opportunity for multi-zone carbon storage and enhanced oil recovery in the Mississippi Interior Salt Basin of Alabama. *Environ. Geosci.* **2008**, *15*, 1–10.
21. NETL. *Best practices for: Terrestrial sequestration of Carbon Dioxide*; **2010**. Available online: <http://www.theclimatehub.com/best-practices-for-terrestrial-sequestration-of-carbon-dioxide> (accessed on October 2015).
22. Levene, H. Robust tests for equality of variances. Olkin, I., Ed.; In *Contributions of Probability and Statistics: Essays in Honor of Harold Hotelling*; Stanford University Press: Palo Alto, CA, USA, **1960**; pp. 278–292.
23. Walsh, P.M.; Nyakatawa, E.Z.; Chen, X.; Dittmar, G.N.; Boelens, T.; Donlon, C.; Walker, S.; Guerra, P.; Jolly, R.; Shepherd, D.; *et al.* Carbon-Dioxide-Enhanced Oil Production from the Citronelle Oil Field in the Rodessa Formation, South Alabama. University of Alabama, Birmingham, AL, USA, 30 April 2011.
24. Chow, F.K.; Granvold, P.W.; Oldenburg, C.M. Modeling the effects of topography and wind on atmospheric dispersion of CO₂ surface leakage at geologic carbon sequestration sites. *Energy Procedia* **2009**, *1*, 1925–1932.

25. Dodds, K.; Daley, T.; Freifeld, B.; Urosevic, M.; Kepic, A.; Sharma, S. Developing a monitoring and verification plan with reference to the Australian Otway CO₂ pilot project. *The Leading Edge* **2010**, *28*, 812–818.

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