

Ocean Sequestration of Crop Residue Carbon: Recycling Fossil Fuel Carbon Back to Deep Sediments

STUART E. STRAND*

College of Forest Resources, 167 Wilcox Hall, Box 352700, University of Washington, Seattle Washington 98195

GREGORY BENFORD

Department of Physics and Astronomy, 4176 Frederick Reines Hall, University of California, Irvine, Irvine, California 92697

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For significant impact any method to remove CO₂ from the atmosphere must process large amounts of carbon efficiently, be repeatable, sequester carbon for thousands of years, be practical, economical and be implemented soon. The only method that meets these criteria is removal of crop residues and burial in the deep ocean. We show here that this method is 92% efficient in sequestration of crop residue carbon while cellulosic ethanol production is only 32% and soil sequestration is about 14% efficient. Deep ocean sequestration can potentially capture 15% of the current global CO₂ annual increase, returning that carbon back to deep sediments, confining the carbon for millennia, while using existing capital infrastructure and technology. Because of these clear advantages, we recommend enhanced research into permanent sequestration of crop residues in the deep ocean.

Introduction

To prevent the potentially disastrous consequences of rising CO₂ levels we must do more than prevent emissions. We must aggressively and permanently (for millennia) remove CO₂ from the atmosphere. World CO₂ levels are accelerating, promising a future with considerable warming and ocean acidification. To confront this crisis all possible methods for reducing CO₂ emissions will be needed, but methods for permanently removing CO₂ from the air will also be essential. All too soon, we will quite plausibly need to reduce CO₂ levels, not just reduce increases.

Significant removal at global scales requires that methods: (1) deal with very large quantities of carbon, (2) sequester the carbon efficiently, and (3) are repeatable over centuries.

Atmospheric CO₂ carbon is accumulating at the rate of about 4–6 Pg (Pg, petagram, 10¹⁵ g, 1 gigaton) per year. For a successful carbon removal technology to have a significant impact on that rate of increase, the technology must remove and sequester at least 0.5 Pg per year (half a “stabilization wedge” (1)) over many years, at least as long as fossil fuel carbon is released to the atmosphere. Technologies that achieve lower rates are worthwhile in that they may have a cumulative effect, but individually they will not significantly

affect atmospheric CO₂ levels. Their individual global impacts will probably always be uncertain, given the other yearly variations in detected CO₂ levels.

There are additional criteria for practically implementing any proposed CO₂ removal method: (4) permanence: securing the carbon sequestered from the atmosphere for thousands of years, (5) no side effects that produce unacceptable environmental damage, (6) rapid and certain implementation, capable of large-scale use within years, not decades (methods demanding lengthy development, or whose success is uncertain, are less desirable than those that are sure, practical, require little research, and can be implemented soon.)

Finally, the best method will also be (7) economical.

No matter how deep our crisis gets, politics and culture will select for economy of effort. Economics will matter, especially among the developing countries.

Capturing Carbon

Because there are only three forms in which carbon can be sequestered (as CO₂, carbonate minerals, and as reduced organic carbon), only a few methods for removing carbon from the atmosphere have been proposed:

- sequestration of crop residue carbon in agricultural soils,
- sequestration in growing forests,
- fertilization of the ocean to promote algal growth,
- alkaline absorption and deep aquifer injection of liquid CO₂, and
- burial of crop residues in the deep ocean (hereafter, CROPS: Crop Residue Oceanic Permanent Sequestration).

We treat these in order.

Soil Sequestration. The first of these methods keeps crop residue in the field to build (sequester) soil carbon. The amount of crop residues available annually depends on many factors related to crop physiology, processing, and conventional utilization techniques, but it can be estimated from the product yield and the harvest index. Table 1 shows the crop residues produced globally and in the United States based on annual yields for 2006 for the most productive crops and their harvest indices. About 5 Pg of total above-ground residues is presently produced from these crops. Dry crop residue biomass contains on average 40% carbon (2, 3), so up to 2 Pg crop residue carbon is produced annually from present agricultural sources. The availability of crop residue from these crops varies widely, dependent on competing uses, but sufficient crop residue is produced to potentially have a significant effect on atmospheric carbon levels.

However, sequestration of aboveground crop residue carbon in soil is inefficient and temporary. In about 20 years, even with no-till practice, less than 10% of the original crop residue carbon remains in the soil (11, 12). Labeled carbon studies show that about 64% of wheat surface crop residue carbon was respired in one year, with a long-term first-order mineralization rate of 3% per year (13). At this rate, over a 20 year period most of the remaining crop residue carbon would be oxidized, leaving about 7% in the soil. Our use of the term carbon sequestration efficiency has its equivalent in the soil science concept of humification or carbon conversion efficiency—the conversion of input carbon in plant form to stable, slowly degrading carbon in the humic fraction of soil. Campbell et al. (1) summarized the carbon conversion efficiency for residues to soil carbon for Canadian prairie soil for 10 and 50 years. Carbon conversion efficiencies ranged from 0 to 25%, or 5 to 30% if best management was adopted.

* Corresponding author phone: 206-543-5350; fax: 206-685-3836; e-mail: sstrand@u.washington.edu.

TABLE 1. Annual Crop Residue Production, Global and United States

crop	harvest index	ref	yield 2006, Pg/year (4)		total crop residue, Pg/year (4)	
			global	U.S.	global	U.S.
maize (corn)	0.53	5	0.699	0.268	0.62	0.237
wheat	0.40	6	0.598	0.049	0.90	0.074
soybeans	0.48	7	0.222	0.088	0.24	0.095
sugar cane	0.39	8	1.39	0.027	2.17	0.042
rice	0.51	9	0.644	0.009	0.62	0.008
sugar beet	0.46	10	0.253	0.031	0.30	0.036
barley	0.52	6	0.139	0.004	0.13	0.004
total					4.98	0.497

Kimble et al. (14) claimed that humification efficiencies for crop residue carbon range from 10 to 20%. Thus estimates of long-term carbon sequestration efficiency for humification of crop residues range from 0 to 30%.

Most estimates of the carbon sequestration potential of agricultural soils are based on the additional accumulation of soil organic matter that occurs in the conversion from conventional tillage to no-till management. Typically change from tillage to no-till would sequester 30–70 g C/m²/yr for up to 10–20 years (14, 15). If the average annual increase in soil carbon in no-till is assumed to be about 40 g C/m²/yr and the average corn yield in the U.S. is about 740 kg grain/m²/yr with a residue harvest index of 0.5 and a carbon content of 40% (2, 3), then the carbon sequestration efficiency of the switch to no-till is about 14%. Recently these types of estimates have been called into question since they are based upon measurements of soil carbon within 30 cm of the surface. If deeper measurements are included the difference in soil carbon between no till and tillage management diminishes in significance and in many cases disappears entirely (11, 16). In any case, humification of crop residues in agricultural soils does not sequester crop residue carbon efficiently, so it does not meet criterion 2.

Marginal agricultural land returned to prairie grassland (17, 18), and prairie wetlands (19), could be significant sinks for atmospheric carbon. Observed sequestration of carbon in restored prairies varies widely, but may average about 33 g C/m²/yr (18, 20). Land available in the U.S. for conversion from agriculture to restoration to prairie can be estimated by the size of the U.S. Conservation Reserve Program, 15 Mha. Thus the maximum expected sequestration rate that could be achieved in the U.S. by conversion to prairie is 0.005 Pg C/yr, an insignificant amount compared to the annual increase in atmospheric C. Restoration of drained agricultural soils to wetlands sequesters higher amounts of carbon, about 300 g C/m²/yr, with the U.S. and Canadian restored wetlands capable of sequestering approximately 0.038 Pg C/yr, far less than the annual increase in atmospheric carbon (19). Thus restoration of prairies from marginal crop land is unlikely to sequester enough carbon to meet criterion 1. There is considerable uncertainty in estimates of how long increases in initial sequestration rates can be sustained in restored prairies; they range from 10 to 60 years (17, 19, 20). After this time no further carbon could be sequestered on the restored wetlands, thus restoration of prairies is not repeatable, so it does not meet criterion 3. Finally, given the pressures to use all agricultural land to meet near future food demands due to population growth, it seems likely that even marginal agricultural land will have higher value for agriculture compared to its use for carbon sequestration. After draining and return to agriculture most of the previously sequestered carbon would be remineralized in a few years. Thus restored prairie is unlikely to meet criterion 4, for permanent sequestration.

Forest Sequestration. By several estimates new forest plantations globally could potentially sequester 0.1–3 Pg

carbon per year (21), possibly meeting criterion 1. But using land for new forests must compete with agriculture and other uses. Once they are mature, forests capture diminishing amounts of carbon (22, 23). With periodic fires, competition for land, and population pressures it is doubtful that most forest carbon will remain sequestered in forest biomass or soil for more than a few decades (21); thus most forest sequestration is not repeatable or permanent, failing criteria 3 and 4.

We also note that wood products taken for construction wood and other uses have a limited lifetime, which we estimate to be on the order of 100 years. While there are instances of wooden structures that have lasted for several hundred years, they are rare because of the recurrence of rot, insect consumption of wood, and fire. Even in cases in which wooden structures have been preserved for centuries because of their cultural significance, the individual timbers have been replaced periodically, and the older wood placed in refuse or burnt. Thus wood products are not a permanent carbon sequestration.

Ocean Fertilization. Fertilization of the ocean could remove 1–2 Pg carbon annually from the atmosphere into marine algal biomass of the upper ocean by some estimates (24), meeting criterion 1; but 60–80% of the fixed carbon appears to remineralize in the water column (24, 25). Thus ocean fertilization is not efficient and fails criterion 2. Possible detrimental environmental effects of large scale fertilization of the upper ocean may be large, so it may fail criterion 5.

Alkaline Absorption. Several groups have proposed forced alkaline absorption of CO₂ directly from the atmosphere, compression of the CO₂, and injection into deep saline aquifers (26, 27). Atmospheric alkaline absorption could extract arbitrarily large amounts of carbon if the requisite facilities were constructed, so it could meet criterion 1. But atmospheric alkaline absorption with deep injection is a complicated technology, capital and energy intensive, and of uncertain safety and permanence. Development to the pilot plant scale will probably take a decade or more. Current thinking focuses on calcination, the process which heats CaCO₃ to make CaO. Estimates for the cost of alkaline absorption from the atmosphere, compression and injection of CO₂ range from 900 \$/t C (base case) to 600 \$/t C (optimized) (28, 29). To remove 10% of the increase in atmospheric CO₂ (0.5 Pg C) would require \$300–450 billion annually. So alkaline scrubbing of the atmosphere would be very expensive; although advances in technology, economies of scale, and use of remote stranded energy may reduce cost. Significant research and development will be required to determine the economic practicality of alkaline absorption and sequestration of CO₂. So forced alkaline absorption is not rapid or certain and is very expensive, failing criteria 6 and 7.

Carbon Sequestration Methods Based on Crop Residue Removal. Other methods for sequestration are based on use of biomass, especially of crop residues, such as corn stover and wheat and soy residues (see Table 1). Since the costs of

their production are paid for by the sale of the crop itself, residues are available inexpensively, and can be processed in the field and moved using the same infrastructure used to process and move the crop products themselves: farm equipment, trucks, trains, and barges. Global large-scale agriculture produces about 2 Pg crop residues C annually. If the average fraction of above-ground crop residue that can be removed sustainably is assumed to be the same as that for corn, 0.3 (3, 30), the global crop residue supply is about 0.6 Pg C. So all uses of crop residues meet criterion 1 of global-scale quantity of source material.

How does removal of crop residues affect soil carbon?

Methods that involve the removal of surface crop residues must account for the effect of such removal on soil organic carbon and erosion. Mineral nutrient loss associated with crop residue removal (primarily N, P, and K) can be replaced by chemical or organic amendments, but the effects of crop residue removal on soil erosion and soil organic matter require a restriction on the amount of aboveground crop residue biomass that can be removed without impacting future crop yields.

Several recent papers have examined the effects of surface crop residue removal on soil erosion and on soil organic matter. Wilhelm et al. (1–3) estimated that 50% of crop residues of corn (stover) could be collected without increasing erosion, if implemented with conservation-based soil management based on local conditions. There is no discernible effect of partial crop residue removal on long-term soil carbon under no-till conditions (4, 5). Removal of 100% of corn stover causes significant short-term loss of soil organic carbon, but no losses were detected for removal fractions less than 70% (6). Corn root biomass, which would be untouched in any proposed crop residue removal protocol, is much more recalcitrant than the aboveground corn stover (31). Reviews of the effects of corn stover removal on soils find that at current corn yields, about 30% of total stover crop residue on average over the American Midwest could be collected without adversely affecting either soil erosion or soil organic carbon levels under no-till or conservation tillage (30, 32). These scenarios assume application of best agricultural management practice to determine how much crop residue can be sustainably removed from a given field (3, 30, 33). Thus, overall aboveground crop residue removals of about 30% probably will not cause unacceptable harm to soils; fulfilling criterion 5.

Cellulosic Ethanol from Crop Residues. Currently the most discussed use for crop residues is for energy production. Ethanol production from cellulose in crop residues is presented as a sustainable source of liquid fuel. The other proposed use is to generate electricity in regional thermal biomass-fired power plants. The disadvantages of biomass use as fuel arise primarily from its low energy density. As well, crop residue contains contaminants that can add to cleaning costs in power plants. Limitations in the efficiencies of current technologies prevent cellulosic ethanol from being a practical fuel source at present, but research into improvements in the technology is ongoing.

Crop Residue Oceanic Permanent Sequestration. The most direct and straightforward method for using crop residues to decrease atmospheric CO₂ levels is the least analyzed: placement of the biomass carbon on deep ocean sediments. As proposed by Metzger and Benford (34), residues would be collected and baled, transported by truck and barge to deep ocean sites, ballasted as needed with stone, and sunk to rest on ocean sediments at depths greater than 1000–1500 m.

Sequestration of biomass residue in the deep ocean is global recycling: terrestrial photosynthesis fixes atmospheric carbon, some of which is fossil fuel-derived, into biomass, which would be sunk in the ocean and eventually buried by

sedimentation, in a process analogous to that by which fossil fuels were formed eons ago. Most carbon in our biosphere lies in such deep sediments, where it has migrated.

Crop residue oceanic permanent sequestration takes advantage of two characteristics of the deep ocean: (1) minimal mixing between the deep sea waters and the upper oceanic layer in contact with the atmosphere (35, 36), and (2) the relative stability of terrestrially derived organic matter in the sediments compared to marine organic matter (37–40), due to the cold, limited oxygen availability, and apparent lack of a marine mechanism for the breakdown of ligno-cellulose equivalent to that of the terrestrial lignin peroxidase systems.

Only one part per thousand of the CO₂ in the deep ocean layer below 1500 m leaks into the upper layer annually, on average (36). Combined with the slow remineralization rate in marine sediments, deep ocean separation from the atmosphere would sequester carbon for thousands of years, thus it meets criterion 4. It also deals with large quantities of carbon and is repeatable for many years, meeting criteria 1 and 3. But how well does it meet criterion 2: how efficient is it at carbon removal?

Carbon Sequestration Efficiency. To assess the effectiveness of carbon removal from the atmosphere we define the carbon sequestration efficiency as

$$\text{CSE} = \frac{\text{Carbon sequestered} - \text{Fossil fuel C emitted during sequestration}}{\text{Crop residue carbon processed}}$$

This concept of the fraction of source carbon that is sequestered in a given process is similar to carbon sequestration efficiency as defined for deep ocean sequestration by fertilization and liquid CO₂ injection (41). We calculated the carbon emitted per ton of crop residues processed during the following activities: nutrient replacement, baling, transportation and barging, and ballast, as shown in Table 2.

The fossil fuel C emitted would total 30 kg per ton crop residue sequestered. The total fossil fuel carbon emitted during the sequestration process would be about 8 t fossil fuel C emitted per 100 t residue C and the carbon sequestration efficiency would be 92%. Thus crop residue sequestration in the deep ocean could fulfill criteria 1 and 2.

Using crop residues to produce cellulosic ethanol or steam for electrical generation does not remove CO₂ from the atmosphere; these technologies are carbon neutral. However, burning residue carbon to produce energy avoids the combustion of fossil fuel carbon, which can remain sequestered underground. We assumed that the fossil fuel carbon not combusted (because cellulosic ethanol is burned) is equivalent to sequestered carbon (52). Thus we define the carbon sequestration efficiency of cellulosic ethanol production as

$$\text{CSE} = \frac{\text{Carbon sequestered} - \text{Fossil fuel C emitted during sequestration} + \text{Fossil fuel C emissions avoided}}{\text{Crop residue carbon processed}}$$

It is important to note that carbon that is sequestered as available fossil fuel should be considered as temporarily sequestered (for decades) (52). As long as society uses fossil fuels, sequestered fuel carbon will be vulnerable to release to the atmosphere.

To estimate the carbon sequestration efficiency of cellulosic ethanol production we used the DOE NREL analysis of Aden et al., 2002 (53). This study modeled ethanol production in a plant using acid prehydrolysis, enzymatic hydrolysis integrated with glucose and xylose fermentation, then distillation, generation of heat for distillation, and production of excess electricity from wastes. This model

TABLE 2. Calculation of the Carbon Emissions Necessary to Remove and Sequester Crop Residues in the Deep Ocean (We arbitrarily chose an average trucking distance of 200 km, an average river shipping distance of 3000 km, representing shipping from the Upper Mississippi River to New Orleans, and an average distance to deep ocean deposition sites of 1000 km)

fuel use during baling, including harvesting (42)			3.50 L diesel/t CR ^a
transportation to barge by tractor trailer (43, 44)	200 km	28 net t CR km/L diesel	7.23 L diesel/t CR
river barging (45)	3000 km	222 net t CR km/L diesel	13.5 L diesel/t CR
ballast required ^b		0.25 t ballast/t CR	
fuel required for extraction and processing (46)		0.93 L diesel/t ballast	0.23 L diesel/t CR
total mass ocean barged ocean barging, with ballast (45)	1000 km	1.25 t ocean barged/t CR 900 net t km/L diesel	1.38 L diesel/t CR
total diesel oil used			25.8 L diesel/t CR
carbon content of diesel			0.73 kg C diesel/L diesel
carbon emitted from diesel use during CROPS			18.9 kg C diesel/t CR
nutrient replacement (47, 48)	N in CR	8.0 kg N/t CR	8.3 kg C for N/t CR
	P in CR	1.8 kg P ₂ O ₅ / t CR	0.28 kg C for P/t CR
	K in CR	8.1 kg K ₂ O/t CR	1.4 kg C for K/t CR
total C emissions for nutrient replacement			9.9 kg C/t CR sequestered
baling plastic, C emissions during manufacture ^c			1.3 kg C emission/t CR sequestered
total carbon emitted			30.1 kg C emitted/t CR sequestered
carbon content of crop residue (2, 3)			40% t CR C/t CR sequestered
total carbon emitted			75.3 kg C emitted/ t CR C sequestered
carbon sequestration efficiency			92.5 t C removed from atmosphere/ 100 t CR C sequestered

^a CR = crop residue. ^b Assuming a compressed bale density of 320 kg per m³, 80% porosity (49), 20% over ballast. ^c Assuming 1 t bales, 1.0 mm polypropylene 10% mesh wrap (50, 51).

projected ethanol production from sugars to be 85–95% efficient and estimated the hydrolysis/fermentation ethanol product concentration to be 5.7%. Both of these percentages are well above those currently obtainable in full-scale reactors.

Using this analysis, ethanol production would avoid 35 t of diesel carbon emissions for every 100 t of residue carbon entering the plant (Table 3). Electricity would be generated from excess heat from ethanol production, avoiding 1.8 t fossil fuel C per 100 t residue C entering the plant. To bale and transport crop residues to the ethanol plant would require emission of approximately 0.9 t diesel carbon per 100 t residue C processed. Finally, nutrient replacement to compensate for soil losses of NPK would require about 0.99 kg C emissions per 100 t residue C processed. Thus, the net carbon sequestration efficiency for cellulosic ethanol production would be 32%. For every 100 t of crop residue carbon used to produce ethanol, about 68 t C would return to the atmosphere and 32 t fossil fuel carbon emissions would be avoided. No net carbon would be removed from the atmosphere by cellulosic ethanol production and combustion as fuel.

To understand the impact of these two uses of crop residues, consider how much carbon would be emitted to the atmosphere if the 0.6 Pg of crop residues that could be sustainably produced annually in large-scale global agriculture were used to produce ethanol versus sequestering in the ocean. If 0.6 Pg global residue carbon were sequestered in the ocean with 92% efficiency, carbon accumulation could be reduced from current accumulation rates by 14%, from 4 to 3.4 Pg C annually, a significant decrease. Alternatively, making ethanol from the global residue cellulose would yield a carbon accumulation reduction of 0.2 Pg, about 5% of the current annual emissions, reducing annual emissions from 4.0 to 3.8 Pg—a much less significant decrease.

Thus, crop residues can be used to significantly reduce future levels of atmospheric carbon by sequestering the residues, rather than generating alternative fuel. Crop residues can also be gathered, dried, and used to generate electrical power thermally. Only 3% of U.S. biomass power production comes from farm waste, because inefficiencies limit its use. This alternative was examined by Keith and Rhodes (55) and Metzger et al. (56) in 2002. Their work showed that crop residue sequestration was much more efficient than biomass power generation at slowing CO₂ accumulation in the atmosphere, unless CO₂ from the thermal power plant was liquefied and injected into deep saline aquifers. As long as fuels exist with higher energy yield-to-carbon content (E/C) ratios than biomass, it will always be more energy efficient and less carbon polluting to sequester the biomass in the deep oceans, and use those fuels with higher E/C ratios for power generation, rather than to burn biomass for power generation.

Both cellulosic ethanol production and liquid CO₂ sequestration are technologies with long projected development times. CO₂ liquification and deep injection has high capital cost and large, uncertain inefficiencies due to the energy expenditure necessary to extract, compress, and inject CO₂, 11–33% of the energy produced by the combustion process that generated the CO₂ (57). Determining the actual efficiencies and evaluating the permanency of deep aquifer storage of CO₂ will require extensive research extending over decades. Regional crop residue power plants will have to be situated over deep aquifers suitable for CO₂ storage. Extensive regional piping of liquid CO₂ will be required in many regions. Constructing regional crop residue power plants will take decades, and the joint requirement for CO₂ injection will require additional decades for research and infrastructure construction. The magnitude of the problem is also daunting.

TABLE 3. Calculation of the Carbon Emissions Avoided by Cellulosic Ethanol Production from Crop Residues (CR)

corn stover feedstock input rate (53)	37.7 t CR C/hr
ethanol production rate (53)	1066 kmol ethanol C/hr
energy density of ethanol	0.17 MW hr/kmol ethanol C
energy production rate, ethanol	182 MW hr/hr
energy density of diesel	13.7 MW hr/t diesel C
diesel emissions avoided by ethanol production	13.3 t CO ₂ C from diesel/hr
excess electricity production (53)	2.73 MW hr/hr
CO ₂ C emission avoided by excess electricity ^a	0.67 t CO ₂ C/hr
total CO ₂ C emission avoided	14.0 t CO ₂ C/hr
carbon emission avoidance efficiency, gross	37.0 t CO ₂ C emission avoided /100 t CR C processed
CO ₂ C emission: baling, transport, nutrient replacement	
baling, including harvesting (42)	3.5 L diesel/t CR processed
transportation to ethanol plant by truck assuming average 200 km (43, 44)	7.2 L diesel/t CR processed
total diesel use for baling and transportation	10.7 L diesel/t CR processed
carbon content of diesel	0.73 kg C/L diesel
diesel C emission during baling and transportation	7.84 kg diesel C emission/t CR processed
baling plastic, C emission during manufacture ^b	1.3 kg C emission/t CR processed
total C emissions for baling and transportation	9.14 kg C emission/t CR processed
nutrient replacement, total for NPK ^b	9.9 kg C emission/t CR processed
total CO ₂ C emissions for baling, transport and nutrient replacement	19 kg C emission/t CR processed
carbon content of crop residue (2, 3)	0.4 g CR C/g CR
total CO ₂ C emissions during baling, transport and for N replacement	4.76 t CO ₂ C emissions 100 t CR C processed
net carbon emission avoidance efficiency	32.2 t CO ₂ C emissions avoided/100 t CR C processed
^a CO ₂ from electricity generation, using petroleum = 0.24 t CO ₂ C/MW hr (54). ^b See Table 2.	

TABLE 4. Calculation of the Carbon Emissions Avoided by Cellulosic Ethanol Production from Crop Residues with Capture of Carbon Dioxide Emissions from Ethanol Plants

CO ₂ emissions from combustion, scrubber vent, aerobic vent, losses (53)	2,036 kmol CO ₂ C/hr 24.4 t C CO ₂ C/hr
corn stover feedstock, crop residue carbon (CR C)	37.7 t CR C/hr
capture efficiency of CO ₂ sequestration process (57)	64.8 t CO ₂ C/100 t CR C processed
C sequestration efficiency compared to feedstock CR C	87% t CO ₂ C captured/t CO ₂ C emission
energy losses during C capture, estimated (57)	56 t CO ₂ C captured/100 t CR C processed
C sequestration efficiency, energy corrected	15% loss due to energy expended during C capture
losses due to transport and injection of liquid CO ₂	48 t CO ₂ C/100 t CR C processed
net C sequestration efficiency, CO ₂ capture compared to feedstock CR	1.9 t diesel C/100 t CO ₂ C injected
net C emission avoidance efficiency due to ethanol production	46 t CO ₂ C sequestered/100 t CR C processed
total carbon sequestration and avoidance efficiency	32.6 t CO ₂ C sequestered/100 t CR C processed 79 t CO ₂ C/100 t CR C processed

Sequestering a tenth of today's global CO₂ emissions would mean erecting an industry to force underground every year a volume of compressed gas larger than the volume of crude oil extracted globally. The petroleum industry took a century to develop its infrastructure. Underground CO₂ sequestration will be a vast enterprise.

Thus use of crop residues as an energy source cannot be implemented rapidly and is of uncertain practicality. It fails criterion 6. In contrast, oceanic sequestration is certain in its effectiveness and could be implemented in less than a decade. Indeed, since most of the infrastructure already exists (trucking, barges, etc.) a major program probably needs only a few years and could be rapidly scaled up by adding to existing equipment.

The carbon sequestration efficiency of cellulosic ethanol production could be increased if CO₂ were captured from the hydrolysis and fermentation process of the cellulosic ethanol plant, then liquefied and injected into deep aquifers. But the carbon in the ethanol cannot be captured during its use as a transportation fuel. We estimate the carbon sequestration efficiency of cellulosic ethanol production with CO₂ sequestration to be likely about 79% (see Table 4). The

carbon sequestration efficiencies of cellulosic ethanol production compared to crop residue sequestration appear in Figure 1.

Environmental Impacts of CROPS. Inevitably, ocean sequestration will have environmental side effects. Crop residue sequestration will likely modify the deep ocean sediment communities where the residue bales descend. The extent and intensity of this impact is presently unknown due to a lack of studies on the degradation of fresh terrestrial biomass in the deep ocean benthic environment. The low nutrient content of the crop residues is likely to decrease their degradation rate and their impact on the benthic environment. It is likely that the interior of the bales will become anaerobic, which will further decrease the degradation rate. Because of the slow degradation rate it is unlikely that sulfate will be exhausted, which may prevent methanogenesis. Importantly, the release of CO₂ from mineralization of terrestrial lignocellulosic carbon in the deep ocean sediment environment is likely to be much slower than the dissolution of liquid CO₂ deposited at depth (62), and thus will have less impact on ocean water pH.

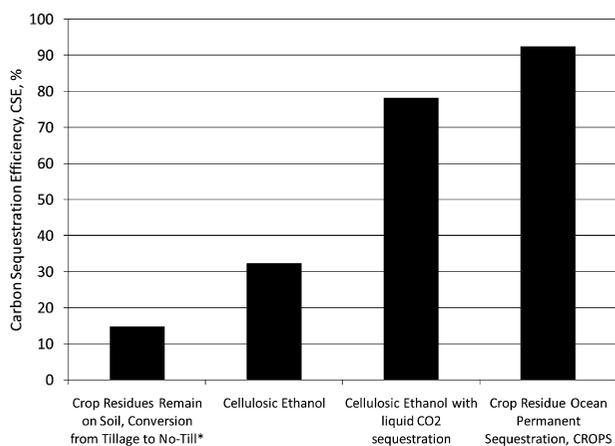


FIGURE 1. How efficient are competing proposed uses of crop residues at sequestering carbon? Carbon sequestration efficiency is the percentage of the crop residue that is sequestered in soil or deep ocean or that avoids fossil carbon emission. *Estimated crop residue carbon remaining in the soil after 20 years (2, 3, 14, 58).

The environmental impact may be minimized by the placement of crop residues in the deep water deposition fan of terrigenous materials on the surface of deep sediments near the mouths of major rivers, such as the deep Gulf of Mexico off the mouth of the Mississippi River, a region of the deep sediment acclimated to terrestrial lignocellulosic inputs (59). Rivers are responsible for large inputs of terrestrial plant organic matter, including fresh plant materials, into deep sediments in the deep ocean, especially during major storms (60, 61). So the ecological communities of terrigenous sediments are likely to be least impacted by crop residue inputs.

Environmental impact may be minimized by concentrating the residue in a compact area. The area required is small compared to the total ocean sediment area. The total annual production of crop residue from large-scale agriculture in the United States is 0.5 Pg dry weight per year (see Table 1). If 30% of the U.S. crop residues were sequestered, 0.15 Pg crop residue per year could be deposited on the ocean floor, a volume of about 1×10^9 m³/year. If the residue were deposited on the sediment in an annual layer 4 m deep, the total sediment area required would be approximately 260 km², about 0.02% of the area of the Gulf of Mexico.

Crop residue ocean sequestration would likely impact a minuscule fraction of the ocean floor, the loss of which must be compared to the great global benefit in reducing and controlling atmospheric CO₂ levels. Thus CROPS may meet criterion 5, minimal environmental side effect, in terms of ocean benthic effects. However, little is known about the

impacts of crop residue sequestration in the ocean. Therefore significant research is needed to determine the sediment area that would be adversely influenced by massive crop residue deposits and how to minimize the environmental damage.

Cost of Ocean Sequestration of Crop Residues. Can CROPS compete in the present carbon markets? In several studies prices of corn stover bales delivered to storage depots from distances up to 180 km averaged 40 \$ per dry t (2006 \$) (43, 45, 63, 64). We estimate the cost of loading of baled crop residue onto the barges and from river barges to ocean barges would cost about 8 \$/t crop residue for each lift. We estimated the waterborne shipping cost for baled crop residue to be 0.018 \$/t/km (2006 \$), based on estimates from grain shippers. Assuming combined river and ocean shipping distance of 4000 km and ballast equal to 25% of the crop residue dry mass, the average shipping cost would be about 74 \$/dry t. The cost of the ballast would be about 7.75 \$/t ballast (65). Total cost would be about 135 \$/t crop residue sequestered. For comparison, bales of biomass delivered by truck and ship 1100 km from Scandinavia to Western Europe were estimated to cost 120 \$/t dry crop residue delivered wet (45). The total cost of CROPS would be 340 \$/t C, or 74 euros/t CO₂ (2006), about twice that of the highest value of carbon on the European market in 2005–2006, 33 euros/t CO₂. These costs do not include some capital costs and the cost of monitoring soil and the ocean deposition sites. If the carbon market were structured to reward sequestration methods with longer sequestration times, CROPS could be economically viable.

Summary

Table 5 summarizes our analysis of how the proposed methods for CO₂ removal from the atmosphere fulfill the criteria for successful and significant reductions of global CO₂. Most of the methods we have considered will fail to sequester carbon in the 0.5 Pg quantities needed to have a significant impact on atmospheric carbon levels. Of those that do succeed in capturing large amounts of carbon repeatedly, only crop residue sequestration in the deep ocean can be implemented rapidly and certainly. Crop residue sequestration should be investigated further and its implementation encouraged.

Recent projections by the global scientific community (66) warn of imminent serious global warming consequences and the need for urgent action. Global decisions must be made in real time, with incomplete data, and with limited options to prevent global warming. In this crisis, all ideas must be considered and the consequences of action and inaction weighed.

Here we have shown that crop residue sequestration, CROPS, using existing technology, could reduce annual global

TABLE 5. Comparison of methods for removing carbon from the atmosphere based on criteria for significant effect on atmospheric CO₂ levels

process	essential for significant effect			essential for practicality			desirable
	1 0.5 Pg quantities of source C	2 efficient sequestration	3 repeatable	4 permanent storage	5 minimize side effects	6 rapid & certain	
sequestration of crop residues in soils	Y	N	N	N	Y	Y	Y
sequestration in growing forests	Y	Y	N	N	Y	Y	Y
fertilization of oceans	Y	N	Y	Y	?	N	?
alkaline sorption and CO ₂ injection	Y	Y	Y	?	?	N	N
cellulosic ethanol	Y	N	Y	N	?	N	?
cellulosic ethanol with CO ₂ injection	Y	Y	Y	?	?	N	?
electrical generation from crop residues	Y	N	Y	N	?	N	Y
electrical generation with CO ₂ injection	Y	Y	Y	?	?	N	?
crop residue ocean sequestration	Y	Y	Y	Y	?	Y	?

CO₂ accumulation by up to 15%. No other use of crop residues or CO₂ sequestration method can make that claim. It is time that oceanic crop residue sequestration is given a serious and balanced role in future planning of how to reduce and control atmospheric carbon levels. Otherwise, we may overlook a powerful tool in the fight against rising atmospheric CO₂.

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Literature Cited

- Pacala, S.; Socolow, R. Stabilization wedges: Solving the climate problem for the next 50 years with current technologies. *Science* **2004**, *305* (5686), 968–972.
- USDA-NASS. *Corn, Field. National Statistics*; <http://www.nass.usda.gov/QuickStats/index2.jsp#top> (Oct. 8, 2008).
- Graham, R. L.; Nelson, R.; Sheehan, J.; Perlack, R. D.; Wright, L. L. Current and potential US corn stover supplies. *Agron. J.* **2007**, *99* (1), 1–11.
- FAO. *FAO Statistical Yearbook*; 2004.
- Kemalian, A. R.; Stockle, C. O.; Huggins, D. R.; Viegas, L. M. A simple method to estimate harvest index in grain crops. *Field Crops Res.* **2007**, *103* (3), 208–216.
- Peltonen-Sainio, P.; Muurinen, S.; Rajala, A.; Jauhiainen, L. Variation in harvest index of modern spring barley, oat and wheat cultivars adapted to northern growing conditions. *J. Agric. Sci.* **2008**, *146*, 35–47.
- Bishnoi, U. R.; Kaur, G.; Khan, M. H. Calcium, phosphorus, and harvest stages effects soybean seed production and quality. *J. Plant Nutr.* **2007**, *30* (10–12), 2119–2127.
- Muchow, R. C.; Robertson, M. J.; Wood, A. W. Growth of sugarcane under high input conditions in tropical Australia 0.2. Sucrose accumulation and commercial yield. *Field Crops Res.* **1996**, *48* (1), 27–36.
- Fageria, N. K. Yield physiology of rice. *J. Plant Nutr.* **2007**, *30* (4–6), 843–879.
- Ober, E. S.; Clark, C. J. A.; Le Bloa, M.; Royal, A.; Jaggard, K. W.; Pidgeon, J. D. Assessing the genetic resources to improve drought tolerance in sugar beet: agronomic traits of diverse genotypes under droughted and irrigated conditions. *Field Crops Res.* **2004**, *90* (2–3), 213–234.
- Baker, J. M.; Ochsner, T. E.; Venterea, R. T.; Griffis, T. J. Tillage and soil carbon sequestration - What do we really know. *Agric. Ecosyst. Environ.* **2007**, *118* (1–4), 1–5.
- Pimentel, D.; Hepperly, P.; Hanson, J.; Douds, D.; Seidel, R. Environmental, energetic, and economic comparisons of organic and conventional farming systems. *Bioscience* **2005**, *55* (7), 573–582.
- Gale, W. J.; Cambardella, C. A. Carbon dynamics of surface residue- and root-derived organic matter under simulated no-till. *Soil Sci. Soc. Am. J.* **2000**, *64* (1), 190–195.
- Kimble, J. M.; Lal, R.; Follett, R. F. *Agricultural Practices and Policy Options for Carbon Sequestration: What We Know and Where We Need to Go. In Agricultural Practices and Policies for Carbon Sequestration in Soil*; Kimble, J. M., Lal, R., Follett, R. F., Eds.; CRC Press, Lewis Publishers: Boca Raton, FL, 2002; pp 495–501.
- West, T. O.; Post, W. M. Soil organic carbon sequestration rates by tillage and crop rotation: A global data analysis. *Soil Sci. Soc. Am. J.* **2002**, *66* (6), 1930–1946.
- Johnson, J. M. F.; Franzluebbers, A. J.; Weyers, S. L.; Reicosky, D. C. Agricultural opportunities to mitigate greenhouse gas emissions. *Environ. Pollut.* **2007**, *150* (1), 107–124.
- McLauchlan, K. K.; Hobbie, S. E.; Post, W. M. Conversion from agriculture to grassland builds soil organic matter on decadal timescales. *Ecol. Appl.* **2006**, *16* (1), 143–153.
- Post, W. M.; Kwon, K. C. Soil carbon sequestration and land-use change: processes and potential. *Global Change Biol.* **2000**, *6* (3), 317–327.
- Euliss, N. H.; Gleason, R. A.; Olness, A.; McDougal, R. L.; Murkin, H. R.; Robarts, R. D.; Bourbonniere, R. A.; Warner, B. G. North American prairie wetlands are important nonforested land-based carbon storage sites. *Sci. Total Environ.* **2006**, *361* (1–3), 179–188.
- Kucharik, C. J. Impact of prairie age and soil order on carbon and nitrogen sequestration. *Soil Sci. Soc. Am. J.* **2007**, *71* (2), 430–441.
- Richards, K. R.; Stokes, C. A review of forest carbon sequestration cost studies: A dozen years of research. *Climatic Change* **2004**, *63* (1–2), 1–48.
- Malhi, Y.; Meir, P.; Brown, S. Forests, carbon and global climate. *Philos. Trans. Royal Soc. London, Ser. A* **2002**, *360* (1797), 1567–1591.
- Paul, K. L.; Polglase, P. J.; Richards, G. P. Predicted change in soil carbon following afforestation or reforestation, and analysis of controlling factors by linking a C accounting model (CAMFor) to models of forest growth (3PG), litter decomposition (GENDEC) and soil C turnover (RothC). *Forest Ecol. Manage.* **2003**, *177* (1–3), 485–501.
- Aumont, O.; Bopp, L. Globalizing results from ocean in situ iron fertilization studies. *Global Biogeochem. Cycles* **2006**, *20* (2), GB2017.
- Zeebe, R. E.; Archer, D. Feasibility of ocean fertilization and its impact on future atmospheric CO₂ levels. *Geophys. Res. Lett.* **2005**, *32* (9), .
- Keith, D. W.; Ha-Duong, M.; Stolaroff, J. K. Climate strategy with CO₂ capture from the air. *Climatic Change* **2006**, *74* (1–3), 17–45.
- Elliott, S.; Lackner, K. S.; Ziock, H. J.; Dubey, M. K.; Hanson, H. P.; Barr, S.; Ciszkowski, N. A.; Blake, D. R. Compensation of atmospheric CO₂ buildup through engineered chemical sinkage. *Geophys. Res. Lett.* **2001**, *28* (7), 1235–1238.
- Stolaroff, J. K. *Capturing CO₂ from Ambient Air: a Feasibility Assessment*; Carnegie Mellon University: Pittsburgh PA, 2006.
- Stolaroff, J. K.; Keith, D. W.; Lowry, G. V. Carbon dioxide capture from atmospheric air using sodium hydroxide spray. *Environ. Sci. Technol.* **2008**, *42* (8), 2728–2735.
- Wilhelm, W. W.; Johnson, J. M. E.; Karlen, D. L.; Lightle, D. T. Corn stover to sustain soil organic carbon further constrains biomass supply. *Agron. J.* **2007**, *99* (6), 1665–1667.
- Johnson, J. M. F.; Barbour, N. W.; Weyers, S. L. Chemical composition of crop biomass impacts its decomposition. *Soil Sci. Soc. Am. J.* **2007**, *71* (1), 155–162.
- Johnson, J. M. F.; Allmaras, R. R.; Reicosky, D. C. Estimating source carbon from crop residues, roots and rhizodeposits using the national grain-yield database. *Agron. J.* **2006**, *98* (3), 622–636.
- Wilhelm, W. W.; Johnson, J. M. F.; Hatfield, J. L.; Voorhees, W. B.; Linden, D. R. Crop and soil productivity response to corn residue removal: A literature review. *Agron. J.* **2004**, *96* (1), 1–17.
- Metzger, R. A.; Benford, G. Sequestering of atmospheric carbon through permanent disposal of crop residue. *Climatic Change* **2001**, *49* (1–2), 11–19.
- Hoffert, M. I.; Wey, Y. C.; Callegari, A. J.; Broecker, W. S. Atmospheric response to deep-sea injections of fossil-fuel carbon-dioxide. *Climatic Change* **1979**, *2* (1), 53–68.
- Wilson, T. R. S. The deep ocean disposal of carbon dioxide. *Energy Convers. Manage.* **1992**, *33* (5–8), 627–633.
- Burdige, D. J. Burial of terrestrial organic matter in marine sediments: A re-assessment. *Global Biogeochem. Cycles* **2005**, *19* (4), GB4011.
- Aller, R. C.; Blair, N. E. Early diagenetic remineralization of sedimentary organic C in the Gulf of Papua deltaic complex (Papua New Guinea): Net loss of terrestrial C and diagenetic fractionation of C isotopes. *Geochim. Cosmochim. Acta* **2004**, *68* (8), 1815–1825.
- Hedges, J. I.; Keil, R. G.; Benner, R. What happens to terrestrial organic matter in the ocean? *Org. Geochem.* **1997**, *27* (5–6), 195–212.
- Prahl, F. G.; De Lange, G. J.; Scholten, S.; Cowie, G. L. A case of post-depositional aerobic degradation of terrestrial organic matter in turbidite deposits from the Madeira Abyssal Plain. *Org. Geochem.* **1997**, *27* (3–4), 141–152.
- Mueller, K.; Cao, L.; Caldeira, K.; Jain, A. Differing methods of accounting ocean carbon sequestration efficiency. *J. Geophys. Res. Oceans* **2004**, *109* (C12), C12018.
- Dobbins, C. L. The impact of higher diesel fuel prices on cost of field operations. *Top Farmer Crop Workshop Newsletter*, June 2006.
- Kumar, A.; Sokhansanj, S.; Flynn, P. C. Development of a multicriteria assessment model for ranking biomass feedstock collection and transportation systems. *Appl. Biochem. Biotechnol.* **2006**, *129* (1–3), 71–87.
- Borjesson, P. I. I. Emissions of CO₂ from biomass production and transportation in agriculture and forestry. *Energy Conversion Manage.* **1996**, *37* (6–8), 1235–1240.

- (45) Hamelinck, C. N.; Suurs, R. A. A.; Faaij, A. P. C. International bioenergy transport costs and energy balance. *Biomass Bioenergy* **2005**, *29* (2), 114–134.
- (46) BCS, Inc. *Energy and Environmental Profile of the U.S. Mining Industry*; December 2002.
- (47) Hoskinson, R. L.; Karlen, D. L.; Birrell, S. J.; Radtke, C. W.; Wilhelm, W. W. Engineering, nutrient removal, and feedstock conversion evaluations of four corn stover harvest scenarios. *Biomass Bioenergy* **2007**, *31* (2–3), 126–136.
- (48) Piringer, G.; Steinberg, L. J. Reevaluation of energy use in wheat production in the United States. *J. Ind. Ecol.* **2006**, *10* (1–2), 149–167.
- (49) Kumar, A.; Cameron, J. B.; Flynn, P. C. Pipeline transport of biomass. *Appl. Biochem. Biotechnol.* **2004**, *113–116*, 27–39.
- (50) Nielsen, R. L. Questions Relative to Harvesting & Storing Corn Stover; <http://www.agry.purdue.edu/ext/corn/pubs/agry9509.htm> (URL verified 10/14/08).
- (51) Harding, K. G.; Dennis, J. S.; von Blottnitz, H.; Harrison, S. T. L. Environmental analysis of plastic production processes: Comparing petroleum-based polypropylene and polyethylene with biologically-based poly-beta-hydroxybutyric acid using life cycle analysis. *J. Biotechnol.* **2007**, *130* (1), 57–66.
- (52) Herzog, H.; Caldeira, K.; Reilly, J. An issue of permanence: Assessing the effectiveness of temporary carbon storage. *Climatic Change* **2003**, *59* (3), 293–310.
- (53) Aden, A.; Ruth, M.; Ibsen, K.; Jechura, J.; Neeves, K.; Sheehan, J.; Wallace, B.; Montague, L.; Slayton, A.; Lukas, J. *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover*; NREL/TP-510-32438; National Renewable Energy Laboratory: Golden, CO, June 2002.
- (54) U.S. DOE. *Carbon Dioxide Emissions from the Generation of Electric Power in the United States*; U.S. Department of Energy and U.S. Environmental Protection Agency: Washington, DC, July 2000.
- (55) Keith, D. W.; Rhodes, J. S. Bury, burn or both: A two-for-one deal on biomass carbon and energy - Reply. *Climatic Change* **2002**, *54* (3), 375–377.
- (56) Metzger, R. A.; Benford, G.; Hoffert, M. I. To bury or to burn: Optimum use of crop residues to reduce atmospheric CO₂. *Climatic Change* **2002**, *54* (3), 369–374.
- (57) Rubin, E. S.; Chen, C.; Rao, A. B. Cost and performance of fossil fuel power plants with CO₂ capture and storage. *Energy Policy* **2007**, *35* (9), 4444–4454.
- (58) Campbell, C. A.; McConkey, B. G.; Gameda, S.; Izaurrealde, R. C.; Liang, B. C.; Zentner, R. P.; Sabourin, D. Efficiencies of conversion of residue C to soil C. In *Agricultural Practices and Policies for Carbon Sequestration in Soil*; Kimble, J. M., Lal, R., Follett, R. F., Eds.; CRC Press, Lewis Publishers: Boca Raton, FL, 2002; pp 305–314.
- (59) Waterson, E. J.; Canuel, E. A. Sources of sedimentary organic matter in the Mississippi River and adjacent Gulf of Mexico as revealed by lipid biomarker and delta(13) C-TOC analyses. *Org. Geochem.* **2008**, *39* (4), 422–439.
- (60) Goldsmith, S. T.; Carey, A. E.; Lyons, W. B.; Kao, S. J.; Lee, T. Y.; Chen, J. Extreme storm events, landscape denudation, and carbon sequestration: Typhoon Mindulle, Choshui River, Taiwan. *Geology* **2008**, *36* (6), 483–486.
- (61) Mayorga, E.; Aufdenkampe, A. K.; Masiello, C. A.; Krusche, A. V.; Hedges, J. I.; Quay, P. D.; Richey, J. E.; Brown, T. A. Young organic matter as a source of carbon dioxide outgassing from Amazonian rivers. *Nature* **2005**, *436* (7050), 538–541.
- (62) Brewer, P. G.; Peltzer, E. T.; Friederich, G.; Aya, I.; Yamane, K. Experiments on the ocean sequestration of fossil fuel CO₂: pH measurements and hydrate formation. *Mar. Chem.* **2000**, *72* (2–4), 83–93.
- (63) Glassner, D.; Hettenhaus, J.; Schechinger, T. In *Corn Stover Collection Project*; BioEnergy '98-Expanding Bioenergy Partnerships: Madison, WI, 1998; pp 1100–1110.
- (64) Perlack, R. D.; Turhollow, A. F. Feedstock cost analysis of corn stover residues for further processing. *Energy* **2003**, *28* (14), 1395–1403.
- (65) USGS. *Crushed Stone Statistics and Information*; U.S. Geological Survey, 2007.
- (66) IPCC. *Climate Change 2007*; IPCC: Valencia, Spain, November 2007.

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