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Land Clearing and the Biofuel Carbon Debt

Joseph Fargione, *et al.*

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In view of this light-generating mechanism, the "blue-fluorescent antibody" EP2-19G2 should really be called a "blue-emissive" or "blue-luminescent" antibody.

Because roughly 3 eV of photon energy is stored in the charge-transfer excited state, it is predicted to be both a powerful reductant and oxidant. We examined the redox activity of the charge-transfer state in experiments in which irradiation of EP2-19G2-**1** was followed by flash-freezing, yielding a weak electron paramagnetic resonance signal that is attributable to a neutral tyrosyl radical having a small dihedral angle [fig. S2 (*9*)] (*17*). We suggest that a relatively small population of charge-transfer states decays by electron transfer from a tyrosine to the tryptophan radical cation, a proposal that is supported by our finding that the addition of an electron acceptor, namely $[Co(NH_3)_5Cl]^{2+}$, greatly enhances the radical signal (*17*). It is likely that the stilbene anion radical in the charge-transfer state would be oxidized rapidly by Co(III), leaving the Trp cation radical without its electron-transfer partner. The flash-quench–generated [**1**/$TrpH^{\bullet+}$] cation would then have time to oxidize any nearby protein residue, and our experiments show that tyrosine is the main electron donor.

Charge separation and recombination between a chromophore and tryptophan or tyrosine have been investigated previously in other systems (*18*–*21*). Very efficient fluorescence quenching is observed in most cases. Notably, the loss of fluorescence is due to very rapid charge recombination following femtosecond electron transfer between riboflavin and a parallel, π-stacked tryptophan after electronic excitation of the riboflavin-binding protein (*18*). Similarly, the strong fluorescence of fluorescein is quenched upon binding to antibody 4-4-20 via electron transfer from a parallel, π-stacked tyrosine in the antibody-combining site (*19*, *20*); further, the fluorescence of an anticalin-fluorescein complex is efficiently quenched by rapid electron transfer from either a coplanar tryptophan or tyrosine to singlet excited fluorescein (*21*). We conclude that the very bright blue luminescence of EP2-19G2-**1** is attributable to electron-hole recombination of the Trp:stilbene charge-transfer excited state held in the rigid EP2-19G2 matrix that disfavors nonradiative decay.

Protein luminescence (*22*) only rarely (if ever) occurs by electron-hole recombination in a charge-transfer excited state embedded in a polypeptide matrix. The distinctive photophysical properties of the antibody-stilbene complex have already been exploited in chiral sensing for high-throughput screening for the evaluation of catalysts in asymmetric synthesis (*23*, *24*), sensing mercury (*25*), DNA hybridization assays (*26*, *27*), and for analysis of accessible cysteine residues on viral surfaces (*28*). The programmed generation of antibodies against other chromophores may yield novel protein-ligand systems with similar charge recombination-induced luminescence phenomena and further biosensor applications.

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Land Clearing and the Biofuel Carbon Debt

Joseph Fargione,[1] Jason Hill,[2,3] David Tilman,[2]* Stephen Polasky,[2,3] Peter Hawthorne[2]

Increasing energy use, climate change, and carbon dioxide (CO_2) emissions from fossil fuels make switching to low-carbon fuels a high priority. Biofuels are a potential low-carbon energy source, but whether biofuels offer carbon savings depends on how they are produced. Converting rainforests, peatlands, savannas, or grasslands to produce food crop–based biofuels in Brazil, Southeast Asia, and the United States creates a "biofuel carbon debt" by releasing 17 to 420 times more CO_2 than the annual greenhouse gas (GHG) reductions that these biofuels would provide by displacing fossil fuels. In contrast, biofuels made from waste biomass or from biomass grown on degraded and abandoned agricultural lands planted with perennials incur little or no carbon debt and can offer immediate and sustained GHG advantages.

Demand for alternatives to petroleum is increasing the production of biofuels from food crops such as corn, sugarcane, soybeans, and palms. As a result, land in undisturbed ecosystems, especially in the Americas and Southeast Asia, is being converted to biofuel production as well as to crop production when existing agricultural land is diverted to biofuel production. Such land clearing may be further accelerated by lignocellulosic biofuels,

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which will add to the agricultural land base needed for biofuels, unless those biofuels are produced from crops grown on abandoned agricultural lands or from waste biomass.

Soils and plant biomass are the two largest biologically active stores of terrestrial carbon, together containing ~2.7 times more carbon than the atmosphere (*1*). Converting native habitats to cropland releases CO_2 as a result of burning or microbial decomposition of organic carbon stored in plant biomass and soils. After a rapid release from fire used to clear land or from the decomposition of leaves and fine roots, there is a prolonged period of GHG release as coarse roots and branches decay and as wood products decay or burn (*2–4*).

We call the amount of CO_2 released during the first 50 years of this process the "carbon debt" of land conversion. Over time, biofuels from converted land can repay this carbon debt if their production and combustion have net GHG emissions that are less than the life-cycle emissions of the fossil fuels they displace. Until the carbon debt is repaid, biofuels from converted lands have greater GHG impacts than those of the fossil fuels they displace. For crops with nonbiofuel coproducts (e.g., palm kernel oil and meal, soybean meal, or distillers' dry grains), we partition the carbon debt into a "biofuel carbon debt" and a "coproduct carbon debt" based on the market values of the biofuel and its coproducts (*5*).

We calculate how large biofuel carbon debts are, and how many years are required to repay them, for six different cases of native habitat conversion: Brazilian Amazon to soybean biodiesel, Brazilian Cerrado to soybean biodiesel, Brazilian Cerrado to sugarcane ethanol, Indonesian or Malaysian lowland tropical rainforest to palm biodiesel, Indonesian or Malaysian peatland tropical rainforest to palm biodiesel, and U.S. central grassland to corn ethanol (*5*) (table S1). These cases illustrate current impacts of biofuels on habitat conversion. Indonesia and Malaysia account for 86% of global palm oil production (*6*). Accelerating demand for palm oil is contributing to the 1.5% annual rate of deforestation of tropical rainforests in these nations (*7*). An estimated 27% of concessions for new palm oil plantations are on peatland tropical rainforests, totaling 2.8×10^6 ha in Indonesia (*7*). Brazilian Cerrado is being converted to sugarcane and soybeans, and the Brazilian Amazon is being converted to soybeans (*8–10*). Grassland in the United States, primarily rangeland or former cropland currently retired in conservation programs, is being converted to corn production. Rising prices for corn, wheat, and soybeans could cause a substantial portion of the 1.5×10^7 ha of land currently in the U.S. Conservation Reserve Program to be converted to cropland (*11*).

We estimated carbon debts by calculating the amount of CO_2 released from ecosystem biomass and soils. Our analyses account for the amount of plant carbon released as CO_2 through decomposition and combustion, the amount converted to charcoal (charcoal is not part of the carbon debt because it is recalcitrant to decomposition), and the amount incorporated into

[1]The Nature Conservancy, 1101 West River Parkway, Suite 200, Minneapolis, MN 55415, USA. [2]Department of Ecology, Evolution, and Behavior, University of Minnesota, St. Paul, MN 55108, USA. [3]Department of Applied Economics, University of Minnesota, St. Paul, MN 55108, USA.

*To whom correspondence should be addressed. E-mail: tilman@umn.edu

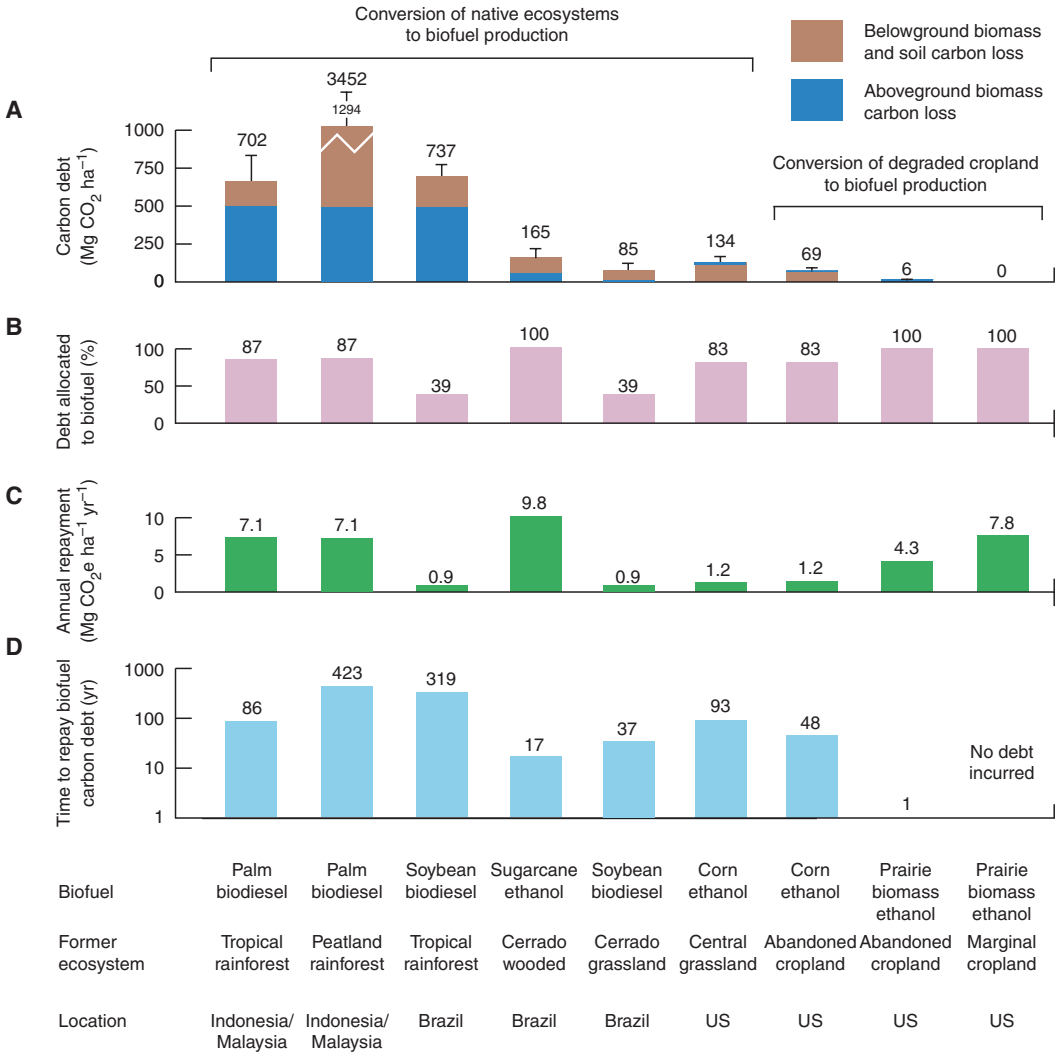

Fig. 1. Carbon debt, biofuel carbon debt allocation, annual carbon repayment rate, and years to repay biofuel carbon debt for nine scenarios of biofuel production. Means and SDs are from Monte Carlo analyses of literature-based estimates of carbon pools and fluxes (*5*). (**A**) Carbon debt, including CO_2 emissions from soils and aboveground and belowground biomass resulting from habitat conversion. (**B**) Proportion of total carbon debt allocated to biofuel production. (**C**) Annual life-cycle GHG reduction from biofuels, including displaced fossil fuels and soil carbon storage. (**D**) Number of years after conversion to biofuel production required for cumulative biofuel GHG reductions, relative to the fossil fuels they displace, to repay the biofuel carbon debt.

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merchantable timber and other long-lived forestry products, which have a half-life of about 30 years (*3*, *12*). Changes in carbon stores caused by land conversion and biofuel production, mainly from accelerated decomposition, were based on evaluation and synthesis of published studies in the relevant ecosystems (*5*). Our estimate of the carbon debt is conservative because timber products continue to decay after 50 years, but this time frame captures most of the carbon debt in systems with mineral soils.

Our results show that converting native ecosystems to biofuel production results in large carbon debts (Fig. 1A). We attribute 13, 61, and 17% of this carbon debt to coproducts for palm, soybeans, and corn, respectively (Fig. 1B) (*5*). The carbon debts attributed to biofuels (quantities of Fig. 1A multiplied by the proportions of Fig. 1B) would not be repaid by the annual carbon repayments from biofuel production (Fig. 1C and table S2) for decades or centuries (Fig. 1D). Converting lowland tropical rainforest in Indonesia and Malaysia to palm biodiesel would result in a biofuel carbon debt of ~610 Mg of CO_2 ha^{-1} that would take ~86 years to repay (Fig. 1D). Until then, producing and using palm biodiesel from this land would cause greater GHG release than would refining and using an energy-equivalent amount of petroleum diesel. Converting tropical peatland rainforest to palm production incurs a similar biofuel carbon debt from vegetation, but the required drainage of peatland causes an additional sustained emission of ~55 Mg of CO_2 ha^{-1} yr^{-1} from oxidative peat decomposition (*5*) (87% attributed to biofuel; 13% to palm kernel oil and meal). After 50 years, the resulting biofuel carbon debt of ~3000 Mg of CO_2 ha^{-1} would require ~420 years to repay. However, peatland of average depth (3 m) could release peat-derived CO_2 for about 120 years (*7*, *13*). Total net carbon released would be ~6000 Mg of CO_2 ha^{-1} over this longer time horizon, which would take over 840 years to repay. Soybean biodiesel produced on converted Amazonian rainforest with a biofuel carbon debt of >280 Mg of CO_2 ha^{-1} would require ~320 years to repay as compared with GHG emissions from petroleum diesel. The biofuel carbon debt from biofuels produced on converted Cerrado is repaid in the least amount of time of the scenarios that we examined. Sugarcane ethanol produced on Cerrado sensu stricto (including Cerrado aberto, Cerrado densu, and Cerradão), which is the wetter and more productive end of this woodland-savanna biome, would take ~17 years to repay the biofuel carbon debt. Soybean biodiesel from the drier, less productive grass-dominated end of the Cerrado biome (Campo limpo and Campo sujo) would take ~37 years. Ethanol from corn produced on newly converted U.S. central grasslands results in a biofuel carbon debt repayment time of ~93 years.

Our analyses suggest that biofuels, if produced on converted land, could, for long periods of time, be much greater net emitters of greenhouse gases than the fossil fuels that they typically displace. All but two—sugarcane ethanol and soybean biodiesel on Cerrado—would generate greater GHG emissions for at least half a century, with several forms of biofuel production from land conversion doing so for centuries. At least for current or developing biofuel technologies, any strategy to reduce GHG emissions that causes land conversion from native ecosystems to cropland is likely to be counterproductive.

We also evaluated the possibility that U.S. cropland that has been retired from annual crop production and planted with perennial grasses may have a short payback time when converted to corn ethanol production, because these systems have already lost a substantial portion of their carbon stores. However, after abandonment from cropping, perennial systems gradually recover their carbon stores. For U.S. central grassland on cropland that has been enrolled in the U.S. Conservation Reserve Program for 15 years, we found that converting it to corn ethanol production creates a biofuel carbon debt that would take ~48 years to repay (Fig. 1D).

If biofuels are to help mitigate global climate change, our results suggest that they need to be produced with little reduction of the storehouses of organic carbon in the soils and vegetation of natural and managed ecosystems. Degraded and abandoned agricultural lands could be used to grow native perennials for biofuel production (*14*, *15*), which could spare the destruction of native ecosystems and reduce GHG emissions (Fig. 1). Diverse mixtures of native grassland perennials growing on degraded soils, particularly mixtures containing both warm-season grasses and legumes, have yield advantages over monocultures (*14*, *16*–*18*), provide GHG advantages from high rates of carbon storage in degraded soils (*14*, *19*), and offer wildlife benefits (*20*). Monocultures of perennial grasses and woody species also can offer GHG advantages over food-based crops, especially if they are sufficiently productive on degraded soils (*21*), as can slash and thinnings from sustainable forestry, animal and municipal wastes, and crop residue (*22*).

Additional factors may influence biofuel impacts on GHG emissions. First, biofuel production can displace crops or pasture from current agricultural lands, indirectly causing GHG release via conversion of native habitat to cropland elsewhere (*23*). Second, improvements in biofuel production could reduce payback times (*24*, *25*). Third, if land cleared for biofuel production had been accruing carbon (we assumed lands were at steady state), the debt would be increased by the loss of this future storage. Fourth, greater biofuel production might decrease overall energy prices, which could increase energy consumption and GHG release (*26*, *27*).

Biofuel production that causes land clearing and GHG release may be favored by landowners who receive payments for biofuels but not for carbon management. Our results suggest that, in order to incorporate the costs of carbon emissions accurately, policy approaches to GHG emission reductions must be extended to include the net GHG emission or sequestration from land-use change. Indeed, the recently enacted U.S. Energy Independence and Security Act of 2007 specifies reductions in life-cycle GHG emissions, including land-use change, relative to a fossil fuel baseline. Moreover, it is important that international policy negotiations to extend the Kyoto Protocol beyond 2012 address emissions from land-use change due to increased demand for biofuels (*28*, *29*).

Our results demonstrate that the net effect of biofuel production via clearing of carbon-rich habitats is to increase CO_2 emissions for decades or centuries relative to the emissions caused by fossil fuel use. Conversely, biofuels from perennials grown on degraded cropland and from waste biomass would minimize habitat destruction, competition with food production, and carbon debts, all of which are associated with direct and indirect land clearing for biofuel production.

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Use of U.S. Croplands for Biofuels Increases Greenhouse Gases Through Emissions from Land-Use Change

Timothy Searchinger,[1]* Ralph Heimlich,[2] R. A. Houghton,[3] Fengxia Dong,[4] Amani Elobeid,[4] Jacinto Fabiosa,[4] Simla Tokgoz,[4] Dermot Hayes,[4] Tun-Hsiang Yu[4]

Most prior studies have found that substituting biofuels for gasoline will reduce greenhouse gases because biofuels sequester carbon through the growth of the feedstock. These analyses have failed to count the carbon emissions that occur as farmers worldwide respond to higher prices and convert forest and grassland to new cropland to replace the grain (or cropland) diverted to biofuels. By using a worldwide agricultural model to estimate emissions from land-use change, we found that corn-based ethanol, instead of producing a 20% savings, nearly doubles greenhouse emissions over 30 years and increases greenhouse gases for 167 years. Biofuels from switchgrass, if grown on U.S. corn lands, increase emissions by 50%. This result raises concerns about large biofuel mandates and highlights the value of using waste products.

Most life-cycle studies have found that replacing gasoline with ethanol modestly reduces greenhouse gases (GHGs) if made from corn and substantially if made from cellulose or sugarcane (*1*–*7*). These studies compare emissions from the separate steps of growing or mining the feedstocks (such as corn or crude oil), refining them into fuel, and burning the fuel in the vehicle. In these stages alone (Table 1), corn and cellulosic ethanol emissions exceed or match those from fossil fuels and therefore produce no greenhouse benefits. But because growing biofuel feedstocks removes carbon dioxide from the atmosphere, biofuels can in theory reduce GHGs relative to fossil fuels. Studies assign biofuels a credit for this sequestration effect, which we call the feedstock carbon uptake credit. It is typically large enough that overall GHG emissions from biofuels are lower than those from fossil fuels, which do not receive such a credit because they take their carbon from the ground.

For most biofuels, growing the feedstock requires land, so the credit represents the carbon benefit of devoting land to biofuels. Unfortunately, by excluding emissions from land-use change, most previous accountings were one-sided because they counted the carbon benefits of using land for biofuels but not the carbon costs, the carbon storage and sequestration sacrificed by diverting land from its existing uses. Without biofuels, the extent of cropland reflects the demand for food and fiber. To produce biofuels, farmers can directly plow up more forest or grassland, which releases to the atmosphere much of the carbon previously stored in plants and soils through decomposition or fire. The loss of maturing forests and grasslands also foregoes ongoing carbon sequestration as plants grow each year, and this foregone sequestration is the equivalent of additional emissions. Alternatively, farmers can divert existing crops or croplands into biofuels, which causes similar emissions indirectly. The diversion triggers higher crop prices, and farmers around the world respond by clearing more forest and grassland to replace crops for feed and food. Studies have confirmed that higher soybean prices accelerate clearing of Brazilian rainforest (*8*). Projected corn ethanol in 2016 would use 43% of the U.S. corn land harvested for grain in 2004 (*1*), overwhelmingly for livestock (*9*), requiring big land-use changes to replace that grain.

Because existing land uses already provide carbon benefits in storage and sequestration (or, in the case of cropland, carbohydrates, proteins, and fats), dedicating land to biofuels can potentially reduce GHGs only if doing so increases the carbon benefit of land. Proper accountings must reflect the net impact on the carbon benefit of land, not merely count the gross benefit of using land for biofuels. Technically, to generate greenhouse benefits, the carbon generated on land to displace fossil fuels (the carbon uptake credit) must exceed the carbon storage and sequestration given up directly or indirectly by changing land uses (the emissions from land-use change) (Table 1).

Many prior studies have acknowledged but failed to count emissions from land-use change because they are difficult to quantify (*1*). One prior quantification lacked formal agricultural modeling and other features of our analysis (*1*, *10*). To estimate land-use changes, we used a worldwide model to project increases in cropland in all major temperate and sugar crops by country or region (as well as changes in dairy and livestock production) in response to a possible increase in U.S. corn ethanol of 56 billion liters above projected levels for 2016 (*11*, *12*). The model's historical supply and demand elasticities were updated to reflect the higher price regime of the past 3 years and to capture expected long-run equilibrium behavior (*1*). The analysis identifies key factors that determine the change in cropland.

1) New crops do not have to replace all corn diverted to ethanol because the ethanol by-product, dry distillers' grains, replaces roughly one-third of the animal feed otherwise diverted.

2) As fuel demand for corn increases and soybean and wheat lands switch to corn, prices increase by 40%, 20%, and 17% for corn, soybeans, and wheat, respectively. These increases modestly depress demand for meat and other grain products beside ethanol, so a small percentage of diverted grain is never replaced.

3) As more American croplands support ethanol, U.S. agricultural exports decline sharply (compared to what they would otherwise be at the time) (corn by 62%, wheat by 31%, soybeans by 28%, pork by 18%, and chicken by 12%).

4) When other countries replace U.S. exports, farmers must generally cultivate more land per ton of crop because of lower yields.

Farmers would also try to boost yields through improved irrigation, drainage, and fertilizer (which have their own environmental effects), but reduced crop rotations and greater reliance on marginal lands would depress yields. Our analysis assumes that present growth trends in yields continue but

[1]Woodrow Wilson School, Princeton University, Princeton, NJ 08544, USA. German Marshall Fund of the United States, Washington, DC 20009, USA. Georgetown Environmental Law and Policy Institute, Washington, DC 20001, USA. [2]Agricultural Conservation Economics, Laurel, MD 20723, USA. [3]Woods Hole Research Center, Falmouth, MA 02540–1644, USA. [4]Center for Agricultural and Rural Development, Iowa State University, Ames, IA 50011, USA.

*To whom correspondence should be addressed. E-mail: tsearchi@princeton.edu

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