

Air Quality Issues Associated with Biofuel Production and Use

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Introduction

Renewable energy policies have promoted rapid growth in the biofuel economy on a global level. Currently, the United States, Brazil, and Europe account for roughly 90 percent of total ethanol and biodiesel production, though that share is expected to decrease as more countries introduce new biofuel programs (Coyle 2007). Malaysia, for example, is now the world's largest palm oil exporter and the second largest palm oil producer. Sugar cane (Brazil) and maize (U.S.) are the most common crops for ethanol production with large differences in energy efficiency between the two production lines. Soy (Brazil and U.S.) and rapeseed (E.U.) are the most common biodiesel feedstocks. In the U.S., liquid biofuel production has grown rapidly from just over 6 billion liters in 2000 to 26.5 billion liters in 2007 (Brown 2008) with a commensurate boom in the number of new ethanol and biodiesel refining plants constructed. The production and use of these fuels produce a range of emissions

from agricultural, industrial, and combustion processes with potential impacts on climate, human health, visibility, and ecosystem productivity. Thus, with the prospect of continued growth and greater international expansion, understanding the air quality impacts of biofuel's growing role is critical to developing informed policies.

This chapter examines the air quality impact of the biofuel life cycle from production to combustion. We restrict our analysis to the impact of biofuels on air quality and particularly on those atmospheric species that have pronounced effects on human health and the environment. We do not examine the impact of biofuels on climate, which is examined in detail in chapters 5 and 6 of this volume (see Menichetti and Otto 2009; Ravindranath et al. 2009), nor do we examine the possible implications on stratospheric ozone depletion. Further, we concentrate on current pathways for the production and use of liquid biofuels,

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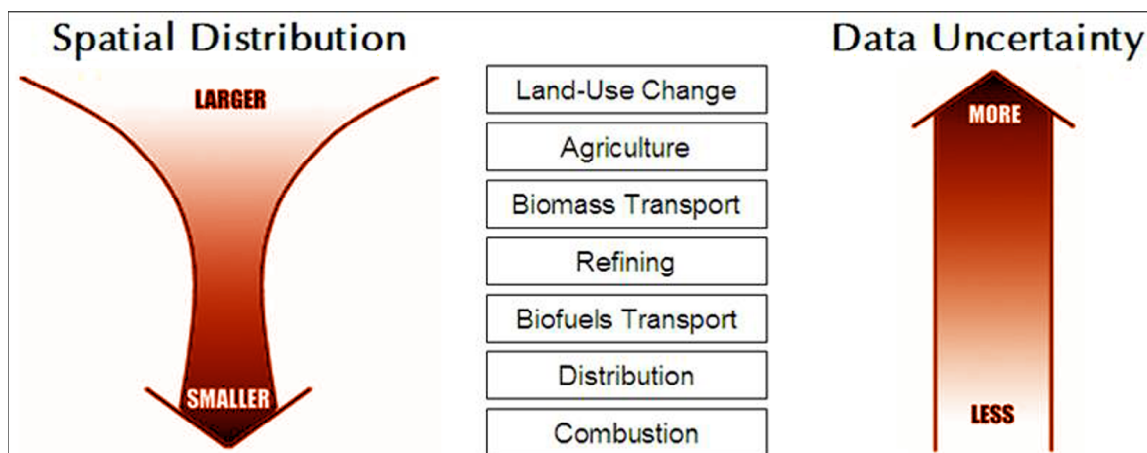


Figure 10.1. The various life cycle stages of biofuel emissions (land use change to combustion). The figure also depicts qualitatively the spatial distribution of emissions and associated level of uncertainty.

though we provide a brief overview of the emissions and impacts of solid biofuels.

The biofuels life cycle spans rural agricultural lands where crops are grown and processed to dense urban cities where biofuels are often combusted (Figure 10.1). All aspects of the production chain can play an important role in subsequent pollutant emissions.

Pollutants undergo a series of complex chemical reactions as they are emitted into the atmosphere. The subsequent chemistry of the pollutants depends on the chemical environment into which they are emitted, which can change on short spatial scales (e.g. from a city to a rural environment). Reactive atmospheric species are either converted into non-reactive species (e.g. carbon dioxide and water), or deposited on the surface of the earth. In some cases, atmospheric reactions may convert relatively innocuous emissions into potentially harmful species (e.g. ozone). The air pollutants produced from the use and manufacture of biofuels generally have relatively short atmospheric lifetimes and are not transported long distances. Their impact is

primarily limited to local (order of 10 km) and regional scales (order of 100-1000 km). As a result, bio-refineries near cities are likely to have larger health impacts than those located in rural areas.

The greenhouse gas (GHG) impacts of biofuel production and use are comparatively well studied; however, the life cycle of air pollutants is different in a number of crucial respects. First, in contrast to GHG emissions, air pollutant impacts tend to be regional in nature. Generally, air pollutants are not sufficiently long-lived to impact the global atmosphere, thus simply knowing the life cycle emissions of air pollutants is not sufficient to characterize their impacts. Second, biofuels claim a GHG credit for the carbon initially absorbed from the atmosphere during feedstock growth. Such a credit is not applicable from an air quality perspective: the combustion of ethanol (or of bagasse) impacts air quality just like the combustion of coal or natural gas. Thus, it is no surprise that an air quality Life Cycle Assessment (LCA) of biofuels differs rather dramatically from one measuring the GHG impacts of biofuels.

That said, few studies have examined the air quality implications of biofuel use from a life cycle perspective. We are aware of only two peer-reviewed studies: Hill et al. (2009) and Jacobson (2009). Other studies include Delucchi (2006), Lane (2006), Beer et al. (2007), SenterNovum (2008) and de Nocker (2008), though it is very likely that there are additional studies of which we are not aware. Even fewer studies have examined the impact of the atmospheric chemical transformations of life cycle biofuel emissions on a regional scale.

To augment the available literature, we examine the life cycle impact of several biofuel pathways (maize-ethanol, switch-grass-ethanol, sugar cane-ethanol, and soy-diesel) using the publicly available GREET (Greenhouse gases, Regulated Emissions and Energy use in Transportation) model (Wang 2007). This model has been used extensively to examine life cycle impacts of biofuels. Details of the assumptions we used in the model are given in box 10.1. As with GHG assessments, large variations are expected in the air quality impacts between different life cycle analyses. Additional studies to extend and refine our knowledge of the impact of biofuels from an air quality perspective are clearly necessary.

In the following section, we review the air pollutants examined and their health and/or environmental effects. Next, we briefly review the use of solid biofuels before analyzing the production chain of the liquid fuels in detail.

Pollutants Examined

The impact of air pollution is most easily understood by examining individual atmospheric species with differentiated emission sources, atmospheric processing,

and impacts. We focus our attention here on five criteria pollutants listed by the U.S. Environmental Protection Agency (EPA): particulate matter, sulfur dioxide, nitrogen oxides, carbon monoxide and ozone. We also discuss volatile organic carbons (an important ozone precursor) and touch on hazardous air pollutants. Below, we provide an overview of these important chemical species and associated human health and/or environmental impacts. For all these, the net impact of biofuel production and use depends on the regional emission environment and the degree to which fossil fuel emissions are replaced.

Particulate Matter (PM). Atmospheric PM, also known as aerosols, is a mixture of very small solid particles and liquid droplets. PM is typically designated as either “inhalable particles” measuring less than 10 microns (PM_{10}), or “fine particles” ($PM_{2.5}$) measuring less than 2.5 micron (EPA 2007a). Whereas PM_{10} is generally “primary” (i.e. directly emitted in particulate form), $PM_{2.5}$ may be either primary or secondary (i.e. formed through chemical reactions in the atmosphere). The smaller particle size of $PM_{2.5}$ means that it may be transported longer distances and poses a greater health impact by penetrating deep into the lungs. This fine PM is primarily associated with combustion, either through direct release of smoke or through the chemical reactions of gaseous combustion emissions (especially NO_x , SO_2 and VOCs). Respiratory health effects of $PM_{2.5}$ exposure include decreased lung function, irregular heartbeat, the onset of asthma, development of chronic bronchitis, non-fatal heart attacks, and possibly premature death in people with heart or lung disease (EPA 2007b).

Carbon Monoxide (CO). CO is a colorless odorless gas released by the incomplete

box 10.1

Model Assumptions

The following provides a summary of the key GREET model assumptions that we used in this study. In this analysis we do not consider the costs to buy or maintain farm machinery or to construct bio-refineries, nor do we consider new technologies for air pollution mitigation.

Farming: Farming energy and fertilizer use by feedstock are summarized in Table 10.1.

Fuel Production: Maize-ethanol yields were set at 2.72 and 2.62 gallons ethanol bushel⁻¹ of maize for dry milling plants (DMP) and wet milling plants (WMP), respectively. DMP were assumed to have an 87.5% share of maize-ethanol plant types, and WMP a share of 12.5%. Co-product credits for maize-ethanol were calculated using the displacement method, in which the amount of displaced maize, soybean meal, N-Urea, and soybean oil were calculated.

Herbaceous ethanol yield was set at 95.0 gallons dry ton⁻¹, and sugar cane ethanol yield was set at 24.0 gallons wet tonne⁻¹. Sugar cane bagasse was assumed to have a 50% moisture content. Soybean based fuel co-production credits were calculated using the displacement method and calculated emission reductions for displacement of soy meal and soy glycerin. Soybean density was set at 60 lbs bu⁻¹; 5.7 lbs. soybean are required to get 1 lb. soy oil, and the biodiesel yield was set at 0.130 gals biodiesel lb⁻¹ soy oil.

Fuels: The GREET Model simulated emissions from passenger cars are for the target year 2010. A 50% share of reformulated gasoline (RFG) in total gasoline is assumed by volume. Low-level blend ethanol vehicles (E10) have 9.5% ethanol by volume, and flex-fuel vehicles (FFV) have 80.8% ethanol by volume (E85). These values include the standard 5% ethanol additive to gasoline as an oxygenate. The lower heating values (LHV) for all fuels were used in all calculations and are given in Table 10.1.

Table 10.1. Summary of model assumptions for farm energy consumed, fertilizer inputs, fuel production, and LHV.

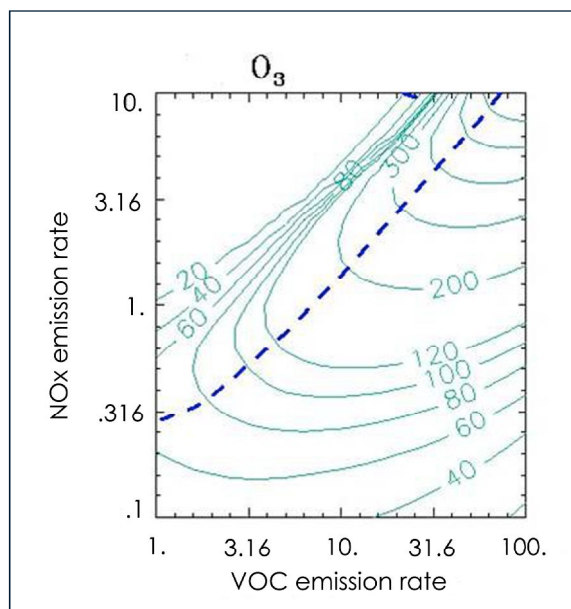
	Farm Energy (Btu)	Nitrogen (g)	P ₂ O ₅ (g)	K ₂ O (g)	CaCO ₃ (g)	Fuel Product (gal)	Fuel LHV (Btu gal ⁻¹)
maize (bushel ⁻¹)	12635	420.0	149.0	174.0	1202.0	2.7/ 2.6	76.3
herbaceous biomass (dry ton ⁻¹)	217230	10635	142.0	226.0	0.0	95	
sugar cane (tonne ⁻¹)	41592	1092	120.8	193.6	5337.7	24	
soy (bushel ⁻¹)	22087	61.2	186.1	325.5	0.0	1.4	119.6

combustion of carbonaceous materials (e.g. fossil fuels, biofuels, and raw biomass). CO poisoning affects the central nervous system and is particularly hazardous to people with heart disease (EPA 2009b). Through a series of chemical reactions, CO emissions can result in ozone production. However, CO is not very reactive and may be transported far from its emission source before it reacts in the atmosphere. Therefore, the resulting ozone production can be widespread.

Nitrogen Oxides (NO and NO₂, known collectively as NO_x). NO_x plays an important role as a precursor in the atmospheric formation of ground-level ozone, PM, and acid rain. The latter occurs through the formation of nitric acid in the atmosphere. Anthropogenic sources of NO_x include all combustion processes (fossil fuel, biofuels, agricultural waste) and, to a lesser extent, the use of fertilizers and subsequent biogenic soil activity. While the immediate impact of NO_x emissions is generally local, the products formed from NO_x may be transported over long distances (EPA 1998).

Volatile Organic Compounds (VOCs). VOCs include a wide range of non-methane hydrocarbons from anthropogenic and natural sources, contributing to ozone formation and PM_{2.5} (as secondary organic aerosols). Anthropogenic VOCs are emitted from a variety of sources including fossil fuel combustion and gasoline evaporation. VOCs are a precursor to aerosol formation and are also an important O₃ precursor (Figure 10.2), although in some circumstances they react with O₃ to reduce its concentration. In particular, ethanol vehicle emissions can be rich in particular forms of VOCs that have important health effects.

Figure 10.2. Ozone (ppbv) Isopleths (green lines) as a function of the average emission rate for NO_x and VOC (10¹² molec m⁻²s⁻¹) Reprinted from Sillman and He 2002



Ozone (O₃). Ground level O₃ is not emitted by air pollution sources directly but is chemically formed in the atmosphere through chemical reactions involving NO_x, CO, and VOCs in the presence of sunlight. As seen in Figure 10.2, the relation between ozone photochemistry and emissions of ozone precursors is nonlinear, leading to a wide variety of emission regimes that are dependent on which primary pollutant (NO_x or VOC) is limiting ozone formation (Sillman and He 2002). This nonlinear behavior makes O₃ formation difficult to estimate from simple scaling of NO_x or VOC emissions and underlines the importance of the chemical background into which the emissions occur. Typically, an O₃ impact assessment requires mathematical models to assess the importance of the various chemical and meteorological processes leading to ozone formation and to calculate the anticipated changes to ambient concentrations associated with emission changes.

Ozone poses a major concern to human health by causing or exacerbating respiratory problems (EPA 1999) and is associated with forest and agricultural degradation with important implications for the world food supply (Chameides et al. 1994).

Sulfur Oxides (collectively referred to as SO_x). Sulfur is present in various amounts in coal and crude oil and is largely released in the form of SO₂ upon combustion or refinement. However, sulfur is generally not present in large quantities in biofuels. Like NO_x, SO_x contributes to PM and acid rain, but it does not directly contribute to O₃ formation or destruction (EPA 2009a).

Hazardous air pollutants (HAPS). Air toxics, also known as HAPs, represent a broad range of chemicals associated with cancer, damage to the immune system, neurological problems, reproductive effects, birth defects, and other serious health concerns, as well as adverse environmental impacts. While some air toxics are naturally emitted (e.g. from volcanic eruptions and forest fires), most are the result of human activities such as fossil fuel combustion and the manufacture and use of chemicals.

Solid Biofuels

Traditional solid biofuel use for heating and cooking has a long history in much of the developing world and wood, charcoal, dung, agricultural wastes, and other local solids continue to be major sources of domestic fuel for rural areas in Africa, India, Indonesia, and other developing countries (Lioussé et al. 1996). Biomass and waste account for over 60% of primary energy use in Sub-Saharan Africa, about 25% in the Asia Pacific region, and about 15% in Latin America and the Caribbean (Goldemberg and Johansson 2004). In these areas, the

resulting pollutant emissions dominate those associated with industry and transportation and impacts tend to be highly localized relative to those of liquid biofuels. The burning of solid biofuels is a significant source of primary black and organic carbon aerosols (Bond et al. 2004) and may also emit significant amounts of O₃ precursors on a regional basis (Yevitch and Logan 2003). Additionally, traditional use of solid biofuels are a major indoor air quality concern due to the high exposures resulting from indoor burning of biomass for cooking and heating. Health impacts include acute lower respiratory infections (ALRI) in childhood, chronic obstructive pulmonary disease (COPD), and chronic bronchitis. The WorldHealth Organization estimates that indoor air pollution accounts for 3.7% of disease in high-mortality developing countries and contributes significantly to childhood acute lower respiratory infections - the leading cause of death for children under age 5 (WHO 2009). However, technology exists to reduce this air pollution at relatively low cost.¹

Solid biofuels can also be combusted to produce heat and electricity in modern facilities. Some biofuel pathways take advantage of solid waste products to supply the energy needed in producing biofuel. For example, the waste product produced from sugar cane, bagasse, is used to fuel Brazilian ethanol plants. Future technology calls for lignin to fuel cellulosic refineries. In modern facilities, emissions from solid biofuels are much reduced over those found in traditional practices.

Liquid Biofuels

The liquid biofuels production life cycle is long and includes land conversion, feed-stock cultivation, transportation to the bio-

refinery, and processing, transportation of the fuel to market, and combustion (Figure 10.1). While in many locations (e.g. Brazil) biofuel use and agricultural production are clearly associated, this is not true everywhere. For example, European biodiesel production in 2007 amounted to over 5,700 tonnes of fuel with over 25 countries contributing to the total (EBB 2007). Since biofuels are produced from different crops, use different agricultural practices with different inputs, and are processed into different fuels, the quantity and impacts of air emissions can vary widely by region, crop, and fuel type. Also, the different types of vehicles using different mixtures of gasoline and biofuel must be accounted for in a life cycle assessment.

Figure 10.1 outlines the various components of the Life Cycle Analysis (LCA) considered in this report. We have grouped these components into 4 assessment categories:

- Emissions from land use change include those associated with direct conversion of agricultural or natural systems to biofuel cropping
- Well-to-pump emissions include those associated with agriculture, biomass transport, refining, biofuels transport, and distribution.
- Mobile source emissions refer to those associated with the combustion of the fuel
- Well-to-wheel emissions refer to the overall emissions indicating the net effect over the entire life cycle

We discuss each category in the sections that follow.

Emissions from Land-Use Changes

Counteracting an expanding demand for agriculture to feed a growing population, agricultural practices have increased in efficiency. For example, agricultural land in the United States has decreased by approximately 13% over the last 50 years, much of it from Midwest agricultural lands (Lubowski et al. 2006). Total agricultural land in most developed countries have decreased or remained constant. Developing countries, especially those in the tropics, are rapidly converting land to agricultural use.

Increased demand for food and fuel has worldwide consequences on land use and has led to an intense ‘food versus fuels’ debate (Young et al. 2009), though the degree of impact varies according to what feedstock is being considered and where it is grown. In the case of Brazil, there is still a very large area of unproductive pasturelands that can be efficiently converted to sugar cane plantation so that the direct impact of ethanol production on food and forested land is considered minimal. Conversely, the association between land clearing and bio-fuels is unequivocal in Southeast Asia, as large amounts of land have been drained and deforested for conversion to oil plantations (Gibbs et al. 2008). Within the U.S., land use has also changed. The surging ethanol demand has led to record high prices for maize, as well as soybeans and other crops, which has increased pressure to plant more acres and potentially convert CRP (Conservation Reserve Program) land to cropland. U.S. maize plantings increased 13% in 2007 (Donner and Kucharik 2007) and have continued to increase; much of the new land has come at the expense of soybean plantings, also a potential biofuel crop

(Donner and Kucharik 2007). Searchinger et al. (2008) suggests that changes in U.S. agricultural practices may create a ripple effect, impacting land use throughout the world.

Land use change has two pronounced impacts on atmospheric emissions and air quality. First, land converted to agriculture is often cleared of vegetation prior to planting via burning, with consequent air quality degradation. Biomass burning has been shown to have severe and widespread air quality ramifications (Bytnerowicz 2008). Second, a more subtle, but long-term effect is the biogenic emission of VOCs. All trees and plants, including agricultural crops, emit VOCs into the atmosphere. The sum of biogenic VOC emissions often dwarfs that from anthropogenic sources, especially in rural areas. Each plant type emits VOCs at different rates depending on temperature and photosynthetic light (Guenther et al. 2005), thus the change in biogenic emissions due to changes in agriculture or vegetative cover at any particular location will depend on what is planted and what vegetation it is replacing. The potential impact of biofuels on VOC emissions through land use change was recognized in the Royal Society Report on biofuels (Royal Society 2008).

We focus our discussion of VOCs on changes in the isoprene, as this is the most abundant biogenic VOC (Kanakidou et al. 2005) and has been well studied. We note in passing, however, that there are also significant monoterpene emissions from vegetation and that these will also likely change with changes in land use. In general, “non-woody” plants and grasses are not known to be important isoprene emitters (Guenther et al. 2005), though grasses are thought to emit more isoprene than crops. We know of no specific measurements

targeting VOC emissions from cellulosic switchgrass feedstocks. Enclosure measurements of maize and sugar cane suggest that these crops do not emit isoprene and that soy is a small emitter (NCAR 2002). Thus, the conversion of broadleaf forested land to agriculture will likely decrease isoprene emissions. Steiner et al. (2002) estimate that conversion of 30% of the forested land area over East China to croplands results in a 34% decrease in biogenic emissions. Anthropogenic disturbance, harvesting, and plantation management is estimated to have had large effects on isoprene emissions in the eastern U.S. during the 1980s and 1990s (Purves et al. 2002) resulting in both positive and negative O₃ changes of a few ppbv (Fiore et al. 2005). Significant changes in dry atmospheric deposition may also be expected with land use change, as deposition to the earth’s surface is impacted by both surface roughness and vegetation type. However, this latter effect has not been well quantified.

Tree plantations of a number of species considered for either cellulosic or biodiesel (e.g. *Populus* (poplar), *Elaeis* (oil palm) and *Salix* (willow)) are significant isoprene emitters. Measurements taken in Southeast Asia indicate that isoprene emissions are four times higher over palm plantations than over the natural forest (Nemitz et al. 2008). Hypothetical scenarios for future extensive tree plantations of high isoprene emitters projected that emissions would increase by a factor of 4 in the Amazon and a factor of 32 over the Northwestern U.S. (Wiedenmyer et al. 2006). The same scenarios predict that O₃ concentrations over the Southwestern U.S. will be increased by as much as 24 ppbv and decreased over Brazil by as much as 7 ppbv. The net effect of the tree plantations on O₃ is sensitive to

the ambient atmospheric chemical concentrations, particularly NO_x .

To conclude, while the air quality impact of biomass burning following land clearing may be large, the impact is normally of short duration (i.e. seasonal). Outside of biomass burning, we are not able to quantitatively or qualitatively assess the impact of biofuels on VOC emissions via land use change. Even the sign of the change is unknown and very much depends on the crop grown. However, we do caution that for tree plantations the impact may potentially be very significant. Expansion of non-woody biofuel crops or grasses is likely to have either a small impact on isoprene or result in isoprene decreases.

Well-to-Pump Emissions

The well-to-pump emissions for biofuels include those emissions associated with growing and transporting the feedstock, producing the fuel, and transporting the fuel to the pump. Here we present the industry-average life cycle from the GREET calculations, though local and regional emission variability is to be expected. The results are weighted on a per-energy basis and expressed as gasoline equivalent liters². As in any life cycle analyses, we cannot account for indirect effects attributable to system-wide shifts in transport and production due to the use of ethanol.

Emissions due to feedstock production and feedstock transport to the bio-refinery.

Processes contributing to the air quality emissions associated with feedstock production include farm practices, fertilizer and pesticide use, and transportation of the feedstock to the bio-refinery. The associated emissions from ethanol (maize, cellulosic, and sugar cane feedstocks) and biodiesel (soy) pathways are compared to emissions

from an equivalent energy content gasoline in Figure 10.3. We assume the feedstock for cellulosic-ethanol is switchgrass.

As shown in Figure 10.3, the air quality impacts of sugar cane are largely attributed to biomass burning. Traditionally, Brazilian sugar cane plantations are harvested after a quick burning to reduce the amount of leaves and facilitate manual harvesting. In 1990, Crutzen and Andreae highlighted the importance of emissions from sugar cane fires to the atmosphere. About 20 tons of biomass per hectare is burned resulting in large aerosol and trace gas emissions with serious consequences on human health (Arbex et al. 2007) and significant effects on the composition and acidity of rainwater over large areas of southern Brazil (Lara et al. 2001; Martinelli et al. 2002). Ozone levels are also expected to be high in regions affected by the burning. Newer facilities have completely mechanized sugar cane harvesting, making large reductions in atmospheric emissions possible. Burning is still a problem though in areas where the terrain is not flat and mechanized harvesting is not possible; in these areas, fields are still burned to aid harvesting (Lara et al. 2001). Conab (2008) estimates that just 30% of the cultivated sugar cane area in Brazil had mechanized harvesting in 2007-2008. Thus, burning of sugar cane remains very problematic from an air quality standpoint. Even burning a small percentage of sugar cane harvest completely overwhelms any other air quality impacts associated with ethanol production. Dramatic improvements would be incurred if agricultural waste-burning is eliminated.

Without agricultural burning, biofuel feedstock emissions from sugar cane production are comparable to those of switchgrass and are much lower those of

maize. The difference is largely due to less intensive farming practices for switchgrass and sugar cane: notably, nitrogen fertilizer inputs for maize are comparatively high. Air quality impacts from inorganic use of nitrogenous fertilizer include emissions from production of the fertilizer, as well as field emissions (i.e. emissions of ammonia and NO_x following fertilizer application). These emissions contribute to acid rain through aerosol formation and to smog through O₃ formation. NO_x emission rates from fertilized soil are highly uncertain as they rely on the microbial conversion of fertilizer to nitrate, which, in turn, is dependent on environmental conditions such as temperature and soil moisture. Rural O₃ concentrations are likely to be very sensitive to local NO_x emissions. Stohl et al. (1996) estimate that soil NO_x emissions in Europe increase O₃ concentrations by an average of 4 ppbv. For the United States, Hall et al. (1996) estimated that two-thirds of the average soil NO_x emissions (not including urban centers) are from fertilized agriculture.

The emissions associated with producing soy feedstock for biodiesel are relatively large. From an air quality standpoint, this phase of the soy-biodiesel life cycle has the largest impact. More energy is required to grow soy than maize, largely because the biodiesel yields per acre for soy are considerably less than the ethanol yields per acre for maize.

Emissions from the bio-refinery and biofuel transport to the pump. GREET calculations for emissions due to the processing of associated feedstocks to ethanol and biodiesel and the subsequent transport of the biofuel to the pump are shown in Figure 10.4. The majority of emissions from the bio-refinery come from the energy fuelling

the boilers used in processing the feedstock. For maize-ethanol, the energy for the boilers is supplied largely from natural gas and coal combustion; for sugar cane-ethanol and cellulosic-ethanol processing fuel can be supplied from the feedstock waste materials (lignin in the case of cellulosic-ethanol or bagasse in the case of sugar cane-ethanol). In a conventional boiler, the use of lignin is likely to yield high emissions of NO_x, hydrocarbons and possibly PM (Unnasch and Chan 2007). Ethanol plants may also emit significant quantities of VOCs from fuel evaporation during storage and transportation and handling of feedstock crops before refining. The handling and transportation of co-product (e.g. dry distillers grain in the case of maize-ethanol and soybean meal in the case of biodiesel) are primary sources of PM₁₀ in ethanol and biodiesel refineries.

To minimize transportation costs embedded in the cost of commercial biofuel production, ethanol and biodiesel refineries are expected to be located in rural areas near the cultivation of the feedstock crops (Brinkman et al. 2005). The rural location of ethanol refineries likely reduces the overall population exposure to emissions, but is also likely to render the resulting O₃ production relatively efficient due to nonlinearities in the O₃ chemistry. Even if emissions are limited with control technologies (e.g. ducting, fans, dust collectors, after burners, and other options), refineries can easily overwhelm all other pollution sources in rural areas (CARE 2007; Burke 2007). In the U.S., large increases in ethanol production may result in large increases in refinery emissions (EPA 2007): increases in VOC and NO_x emissions are estimated at 61 and 83 tons month⁻¹ respectively in the 10% of counties expecting the largest increases in ethanol production. Moreover, as most

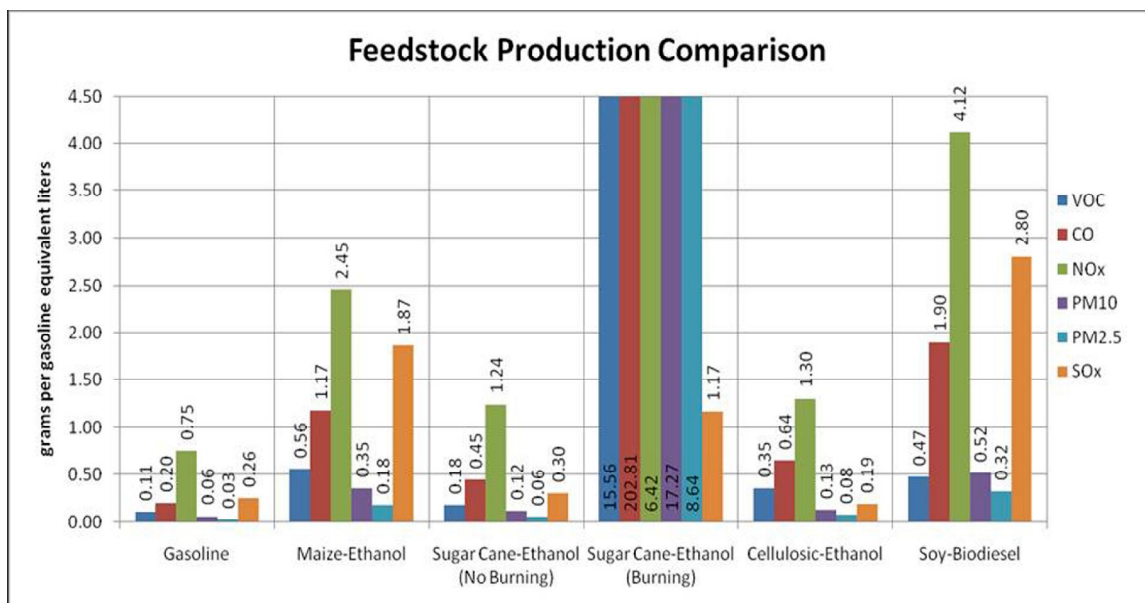


Figure 10.3. Emissions from feedstock production for various energy pathways as calculated by the GREET model.

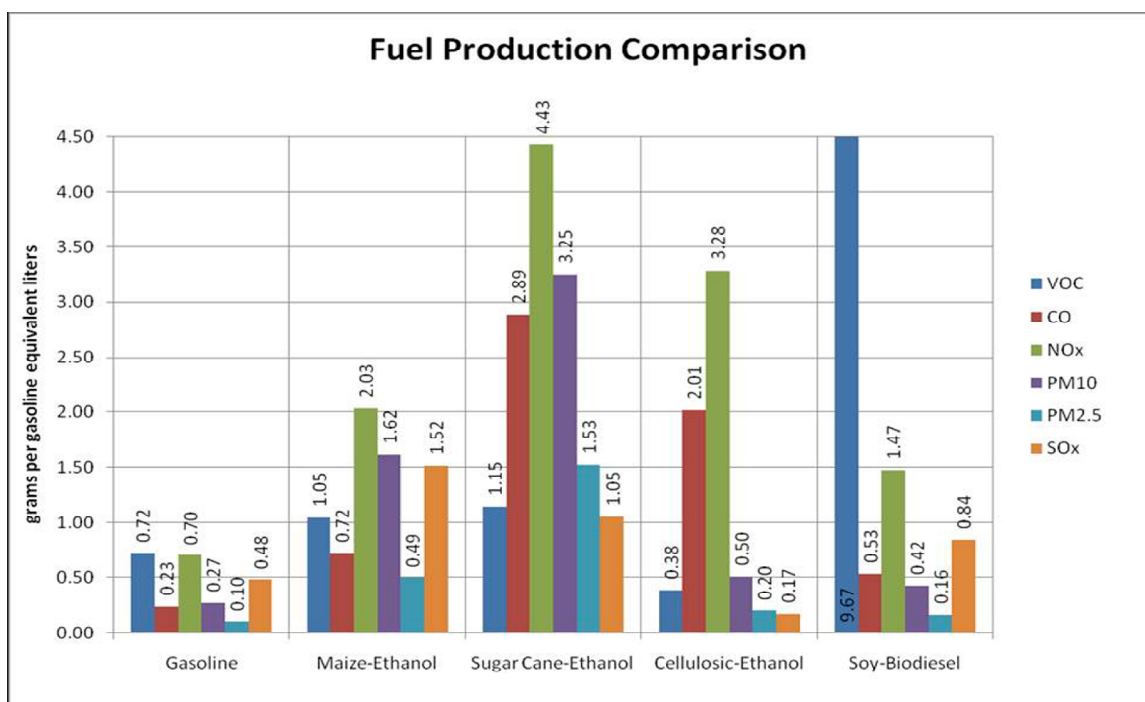


Figure 10.4. Emissions from fuel production and transport to the pump for various energy pathways as calculated by the GREET model.

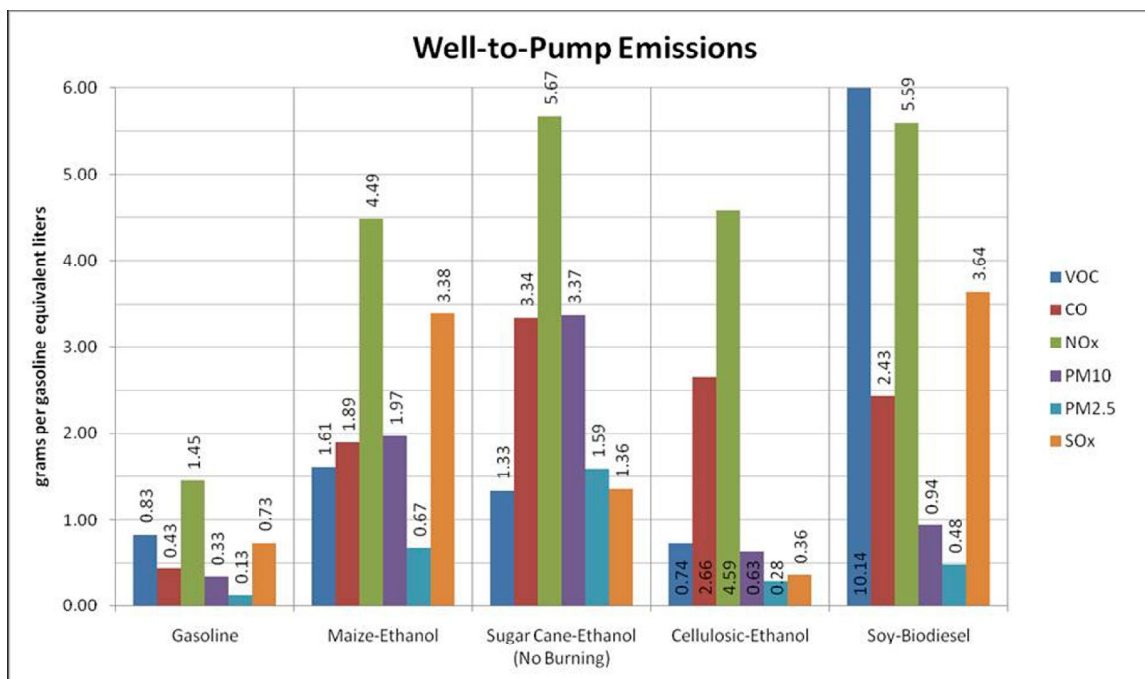


Figure 10.5. Well-to-pump emissions for various energy pathways as calculated by the GREET model. Emissions from the sugar cane ethanol pathway are shown assuming no agricultural burning. No co-product credits are assumed.

biofuels are currently transported by truck or rail, freight transport emissions are expected to increase with growth in biofuels production.

Maize-ethanol refineries are generally more energy intensive than those for gasoline. Consistent with this, the emission of pollutants from maize-ethanol refineries are calculated to be higher than those of gasoline (Figure 10.4). A further increase in refinery emissions is predicted for cellulosic-ethanol, as cellulosic feedstock requires additional energy for ethanol conversion. From a GHG perspective, this additional energy makes little difference: one of the main advantages of switchgrass (and sugar cane) is that the bio-refinery uses feedstock wastes (lignin or bagasse) to power the process. However, this does not help to alleviate the air quality emissions from the bio-refinery.

Figure 10.4 suggests that emissions from sugar cane are higher than those predicted for cellulosic feedstock. According to the GREET model, ethanol transport from refinery to pump accounts for most of the SO₂ emissions and approximately half of the NO_x emissions in this part of the sugar cane life cycle. Particulate emissions are typically high in sugar cane refineries, although mechanical and wet scrubbers are commonly used to control these emissions. At this point, we do not fully understand the differences between sugar cane refineries and the projected cellulosic refineries.

The refining process for biodiesel is fundamentally different from that for ethanol. The extraction of vegetable oil to create biodiesel in large chemical processing plants is typically achieved using hexane - a VOC the U.S. EPA has classified as a hazardous air pollutant - and fugitive emissions may result

from increased biodiesel manufacture. It is important to note that some countries still rely on manual or hydraulic pressing, thus avoiding the emissions associated with hexane. While the production of biodiesel is generally more efficient than that of ethanol, large amounts of VOCs are released (Figure 10.4). The bio-refinery non-VOC emissions from soy-diesel are between 25% and 75% of that from maize-ethanol.

Life cycle upstream emissions. Upstream emissions include emissions from both feedstock and biofuel production (i.e. the well-to-pump emissions) and are reported in Figure 10.5. For sugar cane, we assume an idealistic case where burning is not utilized in the harvest. Upstream emissions of criteria pollutants are also given in Jacobson (2009) and Lane (2006). Jacobson (2009) gives upstream life cycle emissions for maize-E₉₀ (ethanol produced from maize and blended into gasoline at 90%) and cellulosic-E₉₀ (ethanol produced from cellulosic feedstock and blended into gasoline at 90%). These emissions are based on the Lifecycle Emissions Model (LEM) as given in Delucchi (2006). Lane (2006) cal-

culates the upstream emissions for E₁₀₀ produced from wheat in Great Britain.

Table 10.2 summarizes the results of these studies in addition to the GREET results. The considerable variability in emission factors is due to differences in the facilities, agricultural regions, and feedstocks encompassed by the various studies; variability is also introduced by the different ambient environmental conditions and practices in growing the biofuel feedstock and by the different environmental regulations governing biofuel production. Differences in the base-fuel to which the biofuel is compared are an additional source of variability. All life cycle analyses are also subject to variability related to assumptions regarding co-product credits and system boundaries. Uncertainties based on incomplete or poorly quantified input to the life cycle analysis is also expected. For example, data for the emissions from bio-refineries show large differences between state data and GREET estimates (EPA 2007).

Despite the inherent uncertainty, the values reported in Table 10.2 indicate that the

Table 10.2. Upstream emission factors divided by gasoline emission factors for maize-ethanol, cellulosic-ethanol, and wheat ethanol from various sources.

Pollutant	Maize ETOH ¹ (LEM)	Cellulosic ETOH ¹ (LEM)	Maize ETOH (GREET)	Cellulosic ETOH (GREET)	Wheat ETOH ²	Cane ETOH (GREET)
NOX	10.5	5.2	3.1	3.2	>4	3.9
PM	7.0	8.2 ³	6.0 ⁴ -5.1 ⁵	1.9 ⁴ -2.0 ⁵	~7 ⁴	10.2 ⁴ -12.2 ⁵
VOC	5.7	0.7	1.9	0.9	~0.2	1.6
CO	5.8	3.5	4.4	6.6	>10	7.8
SO ₂	1.4	0.7	4.6	0.5		1.9

¹ Jacobsen et al (2009) as calculated by DeLucchi (2006)

² Estimated from figures in Lane et al (2006) for passenger cars

³ Black carbon

⁴ PM₁₀

⁵ PM_{2.5}

upstream emissions of NO_x, CO and PM increase for all biofuel feedstocks compared to gasoline. In both LEM and GREET, the emissions of VOCs and sulfur decrease for cellulosic-ethanol. This decrease in sulfur emissions is expected, as the biofuel feedstock used for combustion in the cellulosic refinery is typically low in sulfur content. Lane (2006) also calculates a decrease in VOC emissions for wheat-ethanol.

Jacobson (2009) calculates that the increase in PM (black carbon) from maize-E90 and cellulosic-E90 systems increase the U.S. death rate by an overall 5.0% and 7.5%, respectively. Hill et al. (2009) also found that PM (PM_{2.5}) from the maize-ethanol life cycle degrades public health in comparison to gasoline, but found that use of cellulosic ethanol ameliorates the health impacts of PM_{2.5} in comparison to gasoline. They attribute this result to the lower life cycle sulfur emissions (an important precursor of aerosols), the lower agricultural costs associated with cellulosic feedstocks, and excess electricity generated from the combustion of lignin, which displaces emissions from coal burning. The net impact of cellulosic ethanol on air quality results from a number of trade-offs which remain highly uncertain. The emissions due to feedstock production are lower than those of maize-ethanol, but bio-refinery emissions are higher. It is also important to note that the calculations assumed for cellulosic ethanol are based on little input data, as cellulosic ethanol has not been produced on a commercial basis to date.

Delucchi (2006) used LEM to compare the upstream emissions of U.S. soy-biodiesel and ultra low sulfur petrol-diesel: biodiesel emissions were found to be almost a factor of 20 higher for CO, 50 for NO_x, 10 for PM (black carbon and organic carbon aerosols)

and slightly less than twice as much for SO₂. Lane (2006) also calculated higher upstream emissions (CO, NO_x, PM, and VOCs) for biodiesel from rapeseed (U.K.) compared to petro-diesel. The increased emissions for NO_x are particularly significant. In contrast, a study from Australia (Beer et al. 2007) suggests that upstream emissions for biodiesel produced from palm, canola, or tallow are roughly comparable with those from ultra-low sulfur diesel: differences are generally within 50%. Reasons for the variable results between these studies are not immediately clear, but may have to do with co-product allocation (see discussion below), the feedstock used to make the biodiesel, and regional differences in agricultural feedstock production.

Biofuel co-products can significantly impact the attribution of emissions, as they are assumed to save emissions elsewhere in the system. The production of both maize and soy biofuels are assumed to have important co-products. Figure 10.6 shows LCA results for well-to-pump emissions for ethanol (maize) and biodiesel (soy) when co-product credits are included. There is no standard method to calculate these credits, although the EPA prefers the displacement method (EPA 2007), in which air pollutant emissions displaced by the product are given as a credit. In the maize-ethanol pathway, co-product credits come from the production of distillers grains (DDGs), which are primarily used as an animal feed for cattle. Accounting for DDGs, as calculated in the GREET model, reduces maize-ethanol emissions 10% to 27% depending on the emitted species, but does not change the overall result. For soy-biodiesel, however, much of the energy used in harvesting soy is devoted to producing biodiesel co-products (glycerol and soybean meal). Including credits for these co-products

substantially reduces the overall impact of the fuel for all emissions except VOCs.

Further compounding uncertainties regarding upstream impacts, many of the studies cited above, including our GREET analysis, do not account for population exposure to emissions and subsequent chemical transformations. Brinkman et al. (2005) partially allows for this by using GREET to calculate the urban air quality emissions associated with biofuels. Their analysis shows that the urban emissions of NO_x, VOC and PM₁₀ decrease when maize or cellulosic-ethanol is compared with gasoline, in contrast to our results. Hill et al. (2009), using a detailed spatial map of emissions to estimate the population weighted health impacts of PM₁₀, suggest that maize-ethanol increases health risks associated with PM. We recommend that additional LCA studies that more accurately assess the health pros and cons associated with the biofuel life cycle using sophisticated air quality models be carried out. Only by consistently monitoring the regional atmospheric chemical transformations of the life cycle emissions can the consequent population health impacts be accurately assessed in different regions.

Mobile-Source Combustion Emissions

In this section, we present a summary of the expected emissions from combustion of E₁₀, E₈₅, and biodiesel as transportation fuels. The U.S. EPA has considerable experience assessing the impact of ethanol on mobile-source emissions due to its common use as a gasoline oxygenate³.

The impact of adding ethanol to fuel modifies the emissions nonlinearly, thus the emission characteristics of a vehicle using E₁₀ cannot be calculated simply by linearly

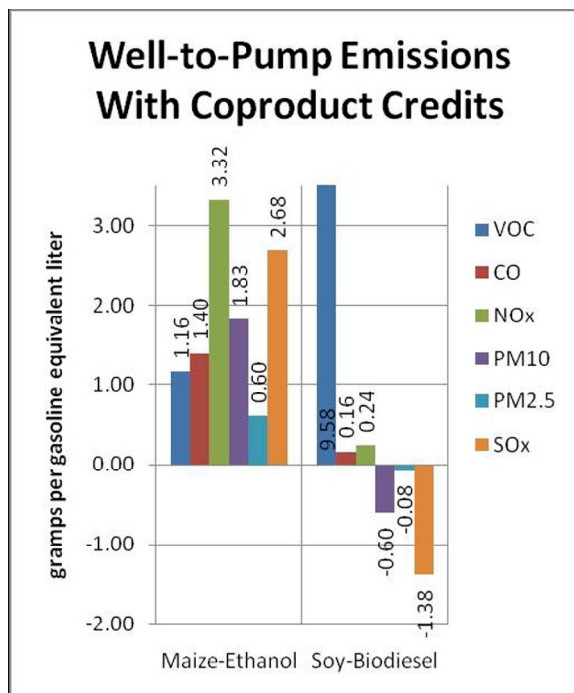


Figure 10.6. Well-to-pump emissions for maize ethanol and soy biodiesel accounting for coproduct credits

weighting E₀ and E₁₀₀ emissions. Laboratory tests have established emissions factors for quantifying how the substitution of biofuels for fossil fuels affects species-specific emissions. It is important to remember, however, that emissions depend on a variety of parameters including type of base-fuel, type and age of vehicle, engine size, presence of control technologies, speed of travel, engine speed, and ambient characteristics like temperature and elevation. In fact, differences due to modifying parameters can be so pronounced that they reverse the sign of the emissions factor. For example, modifications in the base-fuel may completely nullify the impact of adding ethanol. The sensitivity of emissions to this large set of input parameters makes it difficult to quantify the impact of the addition of ethanol to gasoline (Graham et al. 2008; EPA 2007).

E10 and E85. Ethanol blended into gasoline at 10% (E10) is the highest percentage of ethanol currently recommended for automobiles without special modifications within the U.S. Alternatively, flex-fuel vehicles are designed to utilize variable ethanol blends and can burn fuels up to 100% ethanol; however, in many countries, the highest ethanol blends sold consist of 85% ethanol (E85). We, therefore, will concentrate on the emission impacts of E10 and E85.

The U.S. EPA has developed a number of emission models to examine the impact of different gasoline blends under a variety of conditions, though there are important caveats associated with the models and their results. For one, these models work best for tier 0 vehicles (e.g. the 1990 US light duty car fleet) (EPA 2007). Also, the impacts of ethanol on tier 1 and later vehicles (e.g. Transitional Low Emission Vehicle (TLEV), Low Emission Vehicle (LEV) and Ultra Low Emission Vehicle (ULEV)) appear to be sensitive to the fuel blend, but in a manner that has been insufficiently quantified (EPA 2007).

E10 is likely to reduce CO emissions fleet wide (compared to conventional gasoline) due to more complete fuel combustion. EPA (2007) estimates CO savings of 13.8% for tier 0 vehicles and 6.7% for tier 1 and later vehicles. EPA emission models also predict a 7.7% increase in NO_x emissions with E10 (EPA 2007); however, Graham et al. (2008), which examined the impact of E10 over a wide range of vehicles including Tier 1 and LEV vehicles, found no statistically significant increase in NO_x emissions with the addition of ethanol. For VOC emissions, the EPA models suggest a 7.4% decrease in exhaust emissions, but a 30% increase in non-exhaust emissions, due to

Table 10.3. Emission factors for B20 and E85 relative to petro-diesel and gasoline

Pollutant	E85 ¹	E85 ²	B20 ³
NO _x	- 39%	- 30%	+ 2%
PM	- 20%	0	- 10%
VOC	- 4%	+ 22%	- 21%
CO	- 13%	+ 5%	- 11%
SO _x	--	0	--

¹ Battelle (1998); Kelly et al. (1996)

² Jacobson (2007)

³ EPA (2002)

-- not reported

the increased Reid Vapor Pressure⁴ seen in low ethanol blends. This emission increase occurs via increased permeation emissions, whereby fuel molecules migrate through the rubber and plastic parts of the vehicle, and through increased direct fuel evaporation. The net effect is increased VOC emissions with E10. The effect of ethanol on PM emissions is generally inconclusive.

A more exhaustive test of the effect of ethanol is provided by EPA's National Mobile Inventory Model, which includes county specific information on vehicle type, weather conditions and gasoline quality (EPA 2007). In this model, the impact of increased ethanol usage results in decreased CO emissions and increased NO_x and VOC emissions. CARB (2005) and the AIR (2005) found similar results. Note, however, that these model studies are subject to the same uncertainties as previously discussed.

Unfortunately, even less is known about the combustion emission factors of high-

fraction ethanol blends (e.g. E85). Table 10.3 reports changes in emissions from using biofuels in place of reformulated gasoline. The first column gives averaged E85 emissions from multiple EPA trials using Chevy Lumina and Ford Taurus passenger vehicles (Battelle 1998; Kelly et al. 1996). As with tests using E10, there are discrepancies between trials, most notably with emissions of unburned VOCs. Some tests showed as much as a 22% reduction, while others showed a 30% increase. Jacobson (2007) summarized 11 trials examining emissions from E85 use and found, on average, a 30% decrease in NO_x emissions, 5% increase in CO, 22% increase in VOC and no consistent change in PM or SO₂ emissions. Note that these results are not consistent with those of the EPA studies (Table 10.3, second column). Results from a statistical review of the literature on atmospheric emissions from E85 is generally consistent with findings from the Jacobson (2007) study (Graham et al. 2008). In terms of carcinogens, Jacobsen (2007) found an 80% decrease in benzene-related cancers year⁻¹ using E85 and a slight decrease in 1,3-butadiene-related cancers, but a 60% increase in formaldehyde-related cancers and 2000% increase in cancers year⁻¹ related to acetaldehyde emissions. The overall impact on cancer deaths is dependent on the measure used to assess it. Increases in atmospheric acetaldehyde from ethanol use has been established in a number of studies (e.g. Tanner et al. 1988; de Andrade et al. 1998; Martins et al. 2003).

To date, the literature is inconclusive on the net effect of ethanol E85 on O₃ formation. Based on Battelle (1998) and Kelly et al. (1996), O₃ formation potential (OFP) may be reduced by 25%. Jacobson (2007) used a complex photochemical model to predict the formation of O₃ associated with a

hypothetical implementation of E85 in 100% of the gasoline fleet in the U.S.: August O₃ changes ranged from approximately + 4 to - 4 ppbv across the U.S. while O₃ related deaths increased by up to 4%.

A comparative study of the effect of uncombusted and evaporative emissions on O₃ formation with the use of two types of light-duty vehicular fuels presently used in Brazil - gasohol (E20) and 100% hydrated ethanol - suggests that the O₃ peak concentrations are, on average, 28% higher for the hydrated ethanol compared with gasohol. Formation of O₃ from gasohol showed a tendency to start earlier in the day, but, once started, the O₃ creation was much more rapid with hydrated ethanol. These observations indicate a need for more detailed studies regarding the role of unburned fuel emissions and evaporative losses of alcohol and gasohol on the formation mechanisms of atmospheric photochemical oxidants in urban sites, with special attention to the reaction kinetics (Pereira et al. 2004).

Compared to the large difference in upstream emissions between ethanol and gasoline (see Figure 10.3), the downstream emissions differences (i.e. the pump-to-wheel emissions) between these fuels are relatively small (30% at most). Also, for PM, SO₂, and NO_x, the downstream vehicular emissions represent only a fraction of those associated with upstream processes (less than 20%, less than 5%, and less than 50%, respectively) (Delucchi 2003). For VOCs, the downstream emissions may be larger or smaller than those upstream depending on the feedstock. Only for CO are the downstream emissions considerably larger than the upstream ones (by a factors of 3 - 5; Delucchi 2003). The comparatively small difference in mobile source emissions and

the relative importance of upstream processes suggests that, for most species, the upstream life cycle emissions will determine the impact of ethanol vis-à-vis gasoline.

This is not to say that the mobile-source emissions are not important. In certain locations, even small impacts on the O₃ concentration may be critical when assessing compliance with air quality regulations. While the emissions of CO, an O₃ precursor, almost certainly decrease in low-fraction ethanol blends, CO is relatively unreactive and, therefore, contributes little to local O₃ formation. Alternatively, changes in the emissions of NO_x and VOC may be locally significant. Regional O₃ modeling by the EPA suggests that small O₃ increases (less than 1 ppbv) are possible due to changes in mobile emissions associated with the increases in ethanol usage necessary to meet the renewable fuel standards by 2012 (EPA 2007).

Biodiesel. EPA (2002), in one of the most comprehensive studies to date, compared the results of field trials and previous model estimates of biodiesel emission factors at various blends in heavy-duty diesel vehicles (HDDVs). EPA biodiesel emission factors as compared to petroleum diesel are shown in Table 10.3 and indicate that NO_x emissions are likely to increase while PM emissions will likely decrease. Figure 10.7 shows test results for NO_x and PM emissions (EPA 2002). Note that there is considerable variation in the emission factors depending on the particular test. In fact, in some instances differences due to the modifying parameters were so pronounced that they reversed the sign of the B20 emission factor (Fernando et al. 2006; Peterson and Reece 1996), resulting in *decreased* NO_x emissions

and *increased* PM emissions as compared to petrol-diesel.

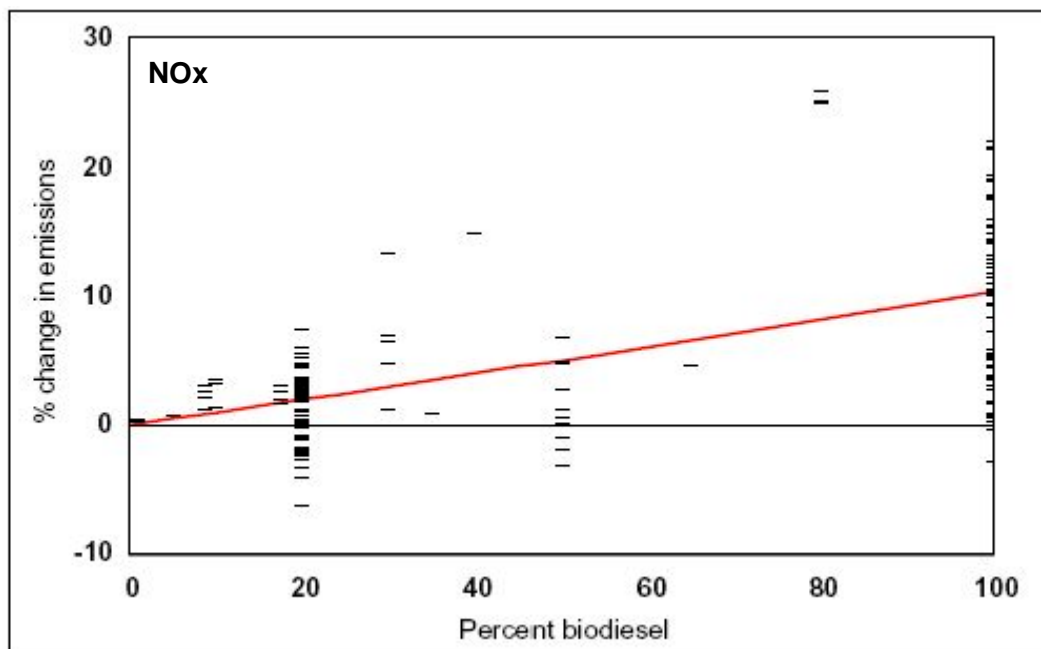
The carcinogenic species formaldehyde and acetaldehyde are major contributors to total carbonyl concentrations (measured up to 4 carbons) emitted from diesel and biodiesel fuel (Guarrieiro et al. 2008). A number of studies have examined carbonyl species emitted from diesel and biodiesel blends with conflicting results (Turrio-Baldassarri et al. 2004; Bikas and Zervas 2007; Corrêa and Arbila 2008). Guarrieiro et al. (2008) suggests that the emissions of all carbonyls except acrolein (a toxic species) and formaldehyde decrease as the blend of biodiesel increases. These results indicate that the Brazilian blending mandate of 2% biodiesel (B2) followed by an increase to B5 will not lead to a significant decrease in carbonyl emissions, but will significantly increase individual emissions of formaldehyde and acrolein.

Ozone formation from the adoption of biodiesel is similarly uncertain. The U.S. Department of Energy's National Renewable Energy Laboratory commissioned a study to model the effects of O₃ formation across several regions and emission regimes assuming a 100% adoption of B20. The use of B20 was found to have "no measurable adverse impact on 1-hour or 8-hour O₃ attainment in Southern California and the Eastern United States." The range of maximum daily effects ranged from estimated increases of +0.26 ppb to decreases of -1.20 ppbv (Morris et al. 2003).

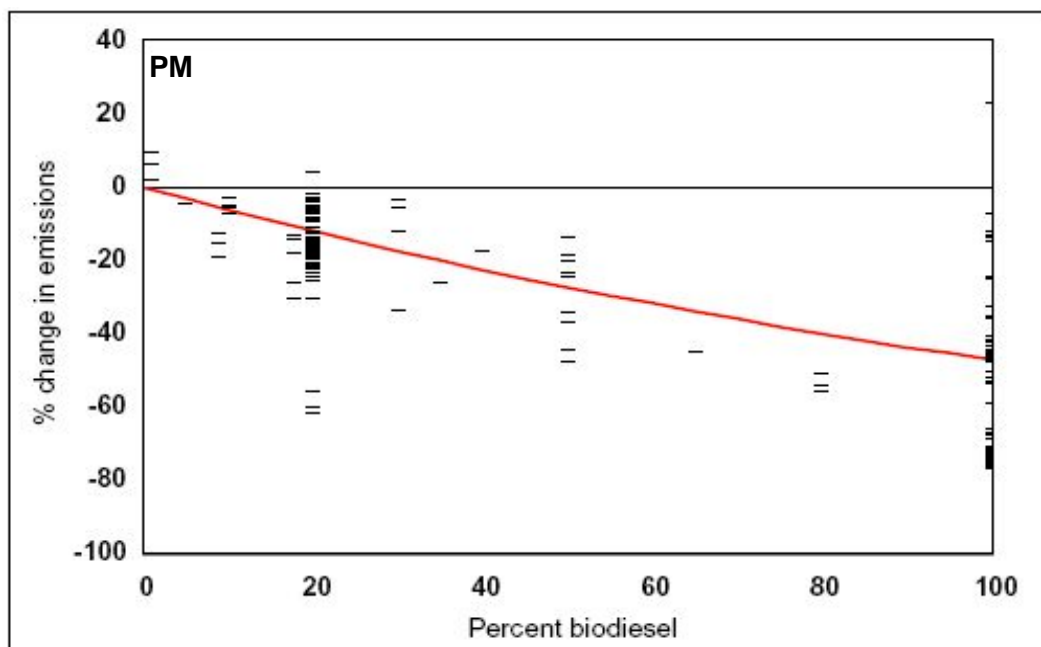
One potential advantage of biodiesel fuels is that they are low in sulfur. In developing countries, there are urban areas in which diesel still contains 100-500 ppm of sulfur. In these regions, the replacement of fossil fuels with sulfur-free biofuels can provide

Figure 10.7. NO_x [a] and PM [b] emissions for biodiesel blends in HDDVs. (Reprinted from EPA 2002).

a



b



an effective means to reduce SO₂ emissions, and thus reduce acid deposition and alleviate atmospheric sulfate, mercaptans (see Machado and Arbilla 2008), and PM concentrations. In the U.S., the sulfur-offset benefits of liquid biofuels may not be significant, as gasoline-fuel vehicles already release negligible amounts of SO₂ and diesel-fueled vehicles are expected to emit significantly lower amounts of SO₂ following the 2007 U.S. Heavy-Duty Highway Rule.

Well-to-Wheel Emissions

Figure 10.8 gives the well-to-wheel lifecycle emissions for maize-ethanol, cellulosic-ethanol and soy-biodiesel as calculated using the GREET model. These emissions

are calculated by adding the transportation emissions associated with each fuel mixture with the weighted combination of the well-to-pump emissions for gasoline (or diesel) and ethanol (or biodiesel) in gasoline equivalent liters.

At low blends (e.g. E10) maize-ethanol and cellulosic-ethanol substantially reduce life cycle CO emissions compared with gasoline (Figure 10.8). This reduction occurs despite the relatively large upstream CO emissions for maize-ethanol due to offsets from tail-pipe emissions. This reduction does not occur for the higher-fraction ethanol blends (e.g. E85) because CO tailpipe emissions are not assumed to decrease for these blends. For the other criteria pollutants (except

Figure 10.8. Changes in well-to-wheel life cycle emissions of various biofuel blends relative to fossil fuels (gasoline or diesel). Mobile source emission factors applied to the GREET model are given in Table 10.4 (E10 and E85) and Table 10.2 (B20). Sulfur emission factors assume that biofuels contain no sulfur. Co-product credits are included in this calculation. Units are in grams per gasoline equivalent liters.

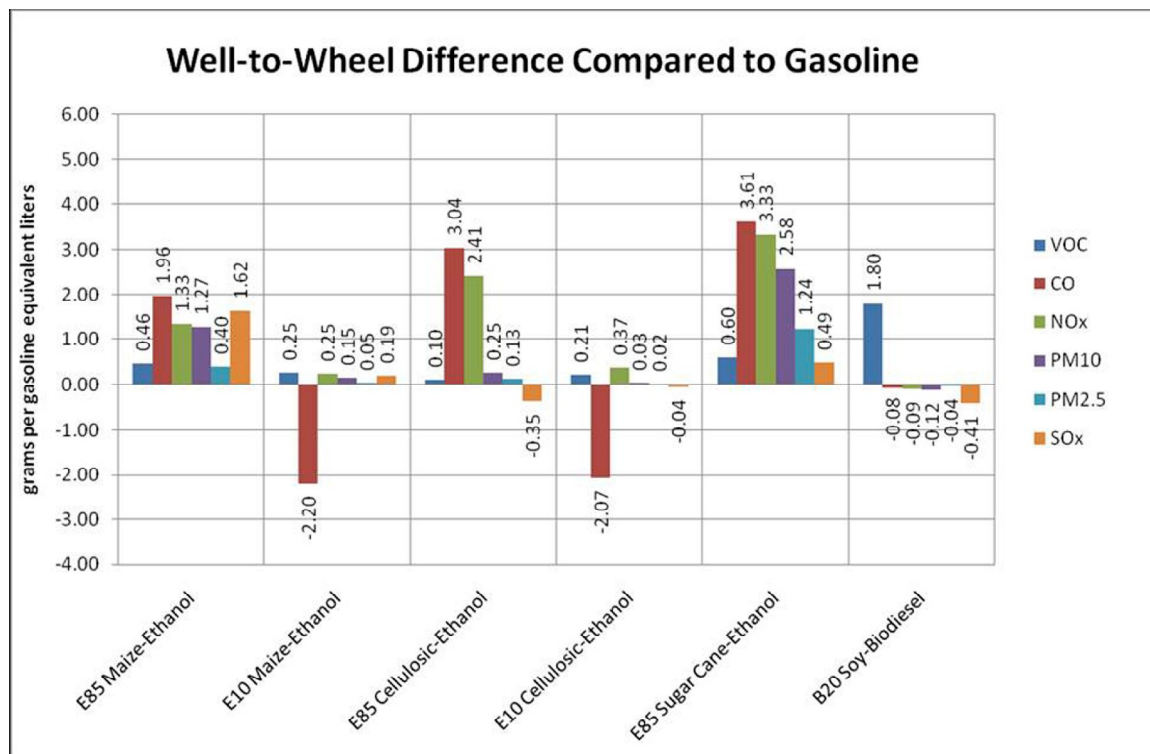


Table 10.4. Mobile source emission factors for E10 and E85 used in the GREET model to calculate well-to-wheel emissions.

	E10*	E85**
NO _x	+ 7%	+ 5%
SO _x	- 10%	- 85%
VOC	+ 20%	+ 2%
CO	- 10%	- 10%
PM _{2.5}	0%	0%
PM ₁₀	0%	0%

*combines EPA estimated for Tier 0 and later vehicles.

** Jacobson 2007.

sulfur for cellulosic-ethanol), the GREET model suggests that bio-ethanol production and use increases life cycle emissions (Figure 10.8). For the most part this is traceable to larger upstream emissions. For VOCs the explanation is more subtle: while the GREET model suggests a decrease in upstream emissions with cellulosic ethanol, down-stream emissions are increased. Lane et al. (2006) finds similar results to those given in Figure 10.8, except that he finds decreased life cycle VOC emissions at high ethanol blends. A study by the Wisconsin Department of Natural Resources (2005) suggests that life cycle emissions associated with an E10 mandate in Wisconsin will increase O₃ by 1-2 ppbv on a typical summer day, mostly due to increased transportation emissions. For sugar cane, the GREET model suggests that, even without biomass burning, E85 from sugar cane increases the emissions of all criteria pollutants. This is primarily due to the emissions from the sugar refinery and subsequent ethanol transport.

Life cycle biodiesel emissions are examined by Lane et al. (2006), Beer et al. (2007), SenterNovum (2008), and de Nocker et al. (2008). The results of these studies differ on whether the life cycle emissions from biodiesel are advantageous over petro-diesel and appear sensitive to the pollutant and the biodiesel feedstock (Beer et al. 2007). Lane et al. (2007) finds biodiesel life cycle emissions are roughly equivalent to diesel except for the case of NO_x and hydrocarbons which are significantly higher (up to approximately 100%). De Nocker et al. (1998) suggests that the life cycle acidification and summer smog potential from rapeseed biodiesel is significantly worse than for petro-diesel, while SenterNovum (2008) finds rapeseed biodiesel improves summer smog, but increases acidification. Our calculations using the GREET model indicate that, except in the case of VOC emissions, the use of biodiesel from soy may reduce pollutant emissions if large co-product credits are included. In light of the high variability of results, the life cycle impact of biodiesel with respect to air pollutants must be regarded as highly uncertain at this point.

Conclusion

We have examined the life cycle pollutant emissions from ethanol and biodiesel and stress that, for a number of reasons, the life cycle assessment of criteria pollutants is considerably different than that for GHGs. For one, in accounting for GHG emissions a credit must be applied due to the original sequestering of carbon by the biofuel feedstock; a similar credit does not apply to pollutant emissions. Secondly, the impact of the air pollutants need to be examined on smaller spatial scales than that used in GHG assessments: due to their short lifetimes, the considered pollutants are not transported

globally and atmospheric chemistry differs on local and regional scales. Thus, while biofuel emissions may act to increase O_3 , in one location, they might have the opposite effect elsewhere. This regionality implies that simply accounting for life cycle pollutant emissions is not sufficient to adequately characterize the impact of biofuels on air quality. Thus, while much of the analysis presented here is a necessary first step, it is not sufficient.

That said, except in the case of CO in low-fraction ethanol blends, we find that maize-ethanol degrades air quality emissions. We believe this is a robust conclusion. While there is no one-to-one correspondence between GHG emissions and those of criteria air pollutants, both should roughly scale with the energy used. Since the production of maize-ethanol requires more energy than the production of petroleum, the result reported here is not surprising. Most air quality studies confirm that maize-ethanol degrades air quality, including the study by Hill et al. (2009), which examined the population weighted life cycle impact of PM on a regional basis.

The energy required to produce ethanol from cellulosic feedstocks is higher than that for maize. The burning of fuels to produce this energy has a substantial impact on the atmospheric emissions of air pollutants. Our analysis using the GREET model suggests that cellulosic fuels tend to increase life cycle emissions relative to gasoline fuel, with the exception of sulfur and CO emissions with low-fraction ethanol blends. In general, life cycle pollutant emissions consist of a balance between the relatively low emissions for feedstock production and the relatively high emissions for fuel production. Hill et al. (2009) found that cellulosic ethanol decreased health impacts

of PM. At this point, the net impact of cellulosic biofuels must be regarded as highly uncertain.

Net air quality is severely impacted by burning of sugar cane even if only a small fraction of the harvested area is burned. Even without agricultural burning, the results presented from the GREET model suggest that ethanol production from sugar cane is worse than that from cellulosic feedstocks. This is primarily due to the relatively large emissions associated with ethanol fuel production and transportation. These results need to be confirmed by other studies, but we see no fundamental reason the net emissions from sugar cane-ethanol are intrinsically higher than for cellulosic feedstocks.

Our calculations with the GREET model suggest that, with allowance for large co-product credits, emissions from the biodiesel life cycle may improve air quality in comparison with petro-diesel. However, the net impact of biodiesel emissions are dependent on the base feedstock and type of co-product credits allowed and results must be regarded as highly uncertain. The studies examined do not appear to have consistent results for biodiesel.

To truly assess the life cycle impact of biofuels on air quality, we recommend additional studies. Sophisticated atmospheric chemistry models are necessary to translate between life cycle emissions, atmospheric concentrations, and local and regional population exposure to pollutants. This is particularly true for O_3 , but also important for the other criteria pollutants. In addition, better quantification of mobile-source emissions in newer vehicles is required.

Notes

- ¹ for example, see project Surya (<http://www-ramanathan.ucsd.edu/ProjectSurya.html>)
- ² ~ 1.5 liters of ethanol is equivalent to a liter of gas
- ³ Ethanol is a fuel oxygenate which has replaced MTBE in recent decades. The addition of oxidants act to decrease CO emissions and fuel oxygenates and new vehicle technology has dramatically reduced the areas within the United States out of compliance with the EPA standard for CO. Amendments to the federal Clean Air Act in the 1990s also mandated the use of reformulated gasoline (RFG) and of oxygenates for areas out of compliance with the National Air Quality Standards for O₃ (EPA 2007), although specific oxidant requirements were removed from RFG formulations in 2006. Somewhat more than half the counties in the federal RFG areas used MBTE as the oxidant of choice in 2004. However, groundwater contamination by MBTE led to MBTE being phased out and replaced by EBTE - an ethanol product (EPA 2007).
- ⁴ Reid Vapor Pressure (RVP) is a common measure of gasoline volatility and a parameter used in estimating fuel tank evaporative losses.

References

- AIR (Air Improvement Resource, Inc). 2005. Emission Reductions from Changes to Gasoline and Diesel Specifications and Diesel Engine Retrofits in the Southeast Michigan Area. Report prepared for SEMCOG (Southeast Michigan Council of Governments), Alliance, and API (American Petroleum Institute). AIR, Inc., Novi MI USA.
- Arbex M.A., L.C. Martins, R.C. de Oliveira, L.A.A. Pereira, F.F. Arbex, J. E.D. Cançado, P. Hilário N. Saldiva, A.L.F. Braga. 2007. *J Epidem Comm Health* 61:395-400.
- Battelle. 1998. Ohio's First Ethanol-Fueled Light-Duty Fleet: Final Study Results. Prepared for USDOE Natl Renewable Energy Lab/ State of Ohio Dept of Admin Services, Columbus OH USA.
- Beer, T., T. Grant, P.K. Campbell. 2007. The greenhouse and air quality emissions of biodiesel blends in Australia, Report Number KS54C/1/F2.29. CSIRO, Clayton S. Vic, Australia
- Bikas, G., E. Zervas. 2007. Nonregulated pollutants emitted from Euro 3 diesel vehicles as a function of their mileage. *Energy and Fuels* 21: 2731-2736
- Bond, T.C., D.G. Streets, K.F. Yarber, S.M. Nelson, J.H. Woo, Z. Klimont. 2004. A technology-based global inventory of black and organic carbon emissions from combustion. *J Geophys Res-Atmos* 109: ARTN D14203
- Brinkman, N., M. Wang, T. Weber, T. Darlington. 2005. Well-to-wheels analysis of advanced fuel vehicle systems: a North American Study of energy use, greenhouse gas emissions, and criteria pollutant emissions. Argonne National Laboratory & General Motors Corporation. (<http://www.transportation.anl.gov/pdfs/TA/339.pdf>)
- Brown, L.R. 2008. Turning to renewable energy. Chapter 12 in Plan B 3.0. Earth Policy Institute, Washington DC.
- Burke, M. 2007. Expert: Ethanol plant could endanger water in aquifer. *The Journal Times* 25 Mar 2007. Racine, WI.
- Bytnerowicz A., M. Arbaugh, A. Riebau, C. Andersen (eds). 2008. Wildland Fires and Air Pollution, 2. Elsevier Amsterdam NL & Oxford GB, 638 pages.
- CARB (California Air Resources Board) 2005. A Summary of the Staff's Assessment Regarding the Effect of Ethanol in California Gasoline on Emissions DRAFT Report. CARB Stationary Source Division/ Criteria Pollutants Branch, Fuels Section Sacramento CA USA
- CARE (Citizens Against Refining Ethanol in Barrie) 2007. Community Impact: A Refinery Could Change Our Community Forever...(<http://www.careinbarrie.com/impact.html>)
- Chameides, W. L., P. S. Kasibhatla, J. Yienger, H. Levy II. 1994. Growth of continental-scale metro-agroplexes, regional ozone pollution, and world food production. *Science* 264(5155): 74-77.
- Conab (Companhia Nacional de Abastecimento) 2007. Perfil do Setor do Açúcar e do Alcool no Brasil, Situação Observada em Novembro de 2007 a Abril/2008. Conab, Brasília BRA.
- Corrêa, S. M. And G. Arbila. 2008. Carbonyl emissions in diesel and biodiesel exhaust. *Atmos Environ* 42: 769-775.
- Coyle, W. 2007. The future of biofuels: a global perspective. *Amber Waves* Nov 2007. USDA Economic Research Service Washington D.C. (<http://www.ers.usda.gov/AmberWaves/November07/Features/Biofuels.htm>)
- Crutzen, P.J. and M.O. Andreae. 1990. Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. *Science* 250: 1669-1678.
- de Andrade, J. B., M.V. Andrade, H.L.C. Pinheiro. 1998. Atmospheric levels of formaldehyde and acetaldehyde and their relationship with the vehicular fleet composition in Salvador, Bahia,

- Brazil. *Journal Brazilian Chemical Society* 9: 219-223.
- de Nocker, C. Spirinckx, R. Torfs. 2008. Comparison of LCA and external-cost analysis for biodiesel and diesel. Presented at the 2nd International conference LCA in Agriculture, Agro-industry and Forestry, 3-4 December 1998 Brussels.
- Delucchi, M. 2006. Lifecycle analyses of biofuels. DRAFT Manuscript. UCD Institute of Transportation Studies Davis, CA USA (www.its.ucdavis.edu/publications/2006/UCD-ITS-RR-06-08.pdf.)
- Donner, S.D. and C.J. Kucharik. 2007. Maize-based ethanol production compromises goal of reducing nitrogen export by the Mississippi River. *PNAS* 105(11): 513-4518.
- EBB (European Union Biodiesel Board). 2009. Statistics: The EU Biodiesel Industry. Last accessed May 2009. <http://www.ebb-eu.org/stats.php>.
- EPA (U.S. Environmental Protection Agency). 1998. NOx: How nitrogen oxides affect the way we live and breathe. EPA-456/F-98-005. Office of Air Quality Planning & Standards, Washington DC.
- EPA (U.S. Environmental Protection Agency). 1999. Ozone and Your Health. EPA-452/F-99-003. Office of Air & Radiation, Washington DC.
- EPA (U.S. Environmental Protection Agency). 2002. A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions. DRAFT Technical Report. EPA420-P-02-001. Office of Air & Radiation, Washington DC.
- EPA (U.S. Environmental Protection Agency). 2007. Regulatory Impact Analysis: Renewable Fuel Standard Program, EPA420-R-07-004.
- EPA (U.S. Environmental Protection Agency). 2009a. Particulate Matter. Last accessed January 2009. <http://www.epa.gov/pm/index.html>.
- EPA (U.S. Environmental Protection Agency). 2009b. Particulate Matter: Health and Environment. Last accessed May 2009. <http://www.epa.gov/air/particulatepollution/health.html>.
- EPA (U.S. Environmental Protection Agency). 2009c. Carbon Monoxide: Health and Environmental Impacts of CO. Last accessed January 2009. <http://www.epa.gov/air/urbanair/co/hlth.html>.
- EPA (U.S. Environmental Protection Agency). 2009d. Sulfur Dioxide: Health and Environmental Impacts of SO₂. Last accessed January 2009. <http://www.epa.gov/air/urbanair/so2/hlth.html>.
- Farrell, A. E., R. J. Plevin, B.T. Turner, A.D. Jones, M. O'Hare, D.M. Kammen. 2006. Ethanol Can Contribute to Energy and Environmental Goals. *Science* 311(5781): 506.
- Fernando, S., C. Hall, S. Jha. 2006. NOx reduction from biodiesel fuels. *Energy & Fuels* 20(1): 376-382.
- Fiore, A.M., L. Horowitz, D.W. Purves, H. Levy II, M.J. Evans, Y. Wang, Q. Li, R.M. Yantosca. 2005. Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States. *J Geophys Res-Atmos* 110: ARTN D12303.
- Gibbs, H.K., M. Johnston, J.A. Foley, T. Holloway, C. Monfreda, N. Ramankutty, D. Zaks. 2008. Carbon payback times for crop-based biofuel expansion in the tropics: the effects of changing yield and technology. *Environ Res Lett* 3(3): 034001.
- Goldemberg, J. and T.B. Johansson (eds). 2004. World Energy Assessment Overview 2004 Update. UNDP Bureau for Development Policy New York, NY (<http://www.undp.org/energy/weaover2004.htm>)
- Graham, L.A., S.L. Belisle, C.L. Bass. 2008. Emissions from light duty gasoline vehicles operating on low blend ethanol gasoline and E85. *Atmospheric Environment* 42: 4498-4516
- Guarieiro, L.L.N., P.A.P. Pereira, E.A. Torres, G.O. da Rocha, J.B. de Andrade. 2008. Carbonyl compounds emitted by a diesel engine filled with diesel and biodiesel-diesel blends: Sampling optimization and emissions profile. *Atmos Environ* 42: 8211-8218
- Guenther, A., T. Karl, P. Harley, C. Wiedinmyer, P.I. Palmer, C. Geron. 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos Chem Phys* 6: 3181-3210.
- Hall, S.J., P.A. Matson, P.M. Roth. 1996. NOx emissions from soil: implications for air quality modeling in agricultural regions. *Annu Rev Energy Environ* 21:311-346.
- Hill J., S. Polasky, E. Nelson, D. Tilman, H. Huod, L. Ludwige, J. Neumann, H. Zhenga, D. Bonta. 2009. Climate change and health costs of air emissions from biofuels and gasoline. *PNAS* 106(6): 2077-2082.
- Huo, H., M. Wang, C. Bloyd, V. Putsche. 2008. Life-cycle assessment of energy and greenhouse gas effects of soybean-derived biodiesel and renewable fuels. ANL/ESD/08-2. Argonne National Laboratory, Energy Systems Division, Argonne IL USA.
- Jacobson, M.Z. 2007. Effects of ethanol (E85) versus gasoline vehicles on cancer and mortality in the United States. *Environ Sci Tech* 41(11): 4150-4157.

- Jacobson, M.Z. 2009. Review of solutions to global warming, air pollution, and energy security. *Energy Environ Sci* 2: 148–173.
- Kanakidou, M., J.H. Seinfeld, S.N. Pandis. 2005. Organic aerosol and global climate modelling: a review. *Atmos Chem Phys* 5: 1053–1123.
- Kelly, K.J., B.K. Bailey, T.C. Coburn, W. Clark, P. Lissiuk. 1996. Federal test procedure emissions test results from ethanol variable-fuel vehicle Chevrolet Lumina. USDOE Natl Renewable Energy Laboratory, Golden CO, USA.
- Lane, B. 2006. Life cycle assessment of vehicle fuels and technologies. Final Report. Ecolane Transport Consultancy on behalf of the London Borough of Camden, Bristol UK.
- Lara, L.B.L.S., P. Artaxo, L.A. Martinelli, R.L. Victoria, P.B. Camargo, A. Krusche, G.P. Ayers, E.S.B. Ferraz, M.V. Ballester. 2001. Chemical composition of rainwater and anthropogenic influences in the Piracicaba river basin, Southeast Brazil. *Atmos Environ* 35: 4937–4945.
- Lara L., P. Artaxo, L.A. Martinelli, P.B. Camargo, R.L. Victoria, E.S.B. Ferraz. 2005. Properties of aerosols from sugar-cane burning emissions in Southeastern Brazil. *Atmospheric Environment* 39: 4627–4637
- Lioussé, C., J.E. Penner, C. Chuang, J.J. Walton, H. Eddleman, H. Cachier. 1996. A global three-dimensional model study of carbonaceous aerosols. *J Geophys Res* 101(19): 411–19, 432.
- Liska A.J., H.S. Yang, V.R. Bremer, T.J. Klopfenstein, D.T. Walters, G.E. Erickson, K.G. Cassman. 2009. Improvements in life cycle energy efficiency and greenhouse gas emissions of maize-ethanol. *J Indust Ecol* :58–74.
- Lubowski, R.N., M. Vesterby, S. Bucholtz, A. Baez, M.J. Roberts. 2006. Major uses of land in the United States 2002. Economic Information Bulletin No. (EIB-14). USDA Economic Research Service, Washington DC.
- Machado, S.C. and G. Arbilla. 2008. Mercaptans emissions in diesel and biodiesel exhaust. *Atmos Environ* 42: 6721–6725.
- Martinelli, L.A., P.B. Camargo, L.B.L.S. Lara, R.L. Victoria, P. Artaxo. 2002. Stable carbon and nitrogen isotope composition of bulk aerosol particles in a C4 plant landscape of Southeast Brazil. *Atmos Environ* 36: 2427–2432.
- Martins, E.M., S.M. Correa, G. Arbilla. 2003. Formaldehyde and acetaldehyde in a high traffic street of Rio de Janeiro, Brazil. *Atmos Environ* 37: 23–29.
- Morris, R.E., A. K. Pollack, G. E. Mansell, C. Lindhjem, Y. Jia, and G. Wilson. 2003. Impact of biodiesel fuels on air quality and human health. NREL/SR-540-33793. USDOE National Renewable Energy Research Laboratory, Golden CO, USA.
- NCAR (National Center for Atmospheric Research). 2002. Biogenic Volatile Organic Compounds (BVOC) Data. Enclosure measurements database. <http://bai.acd.ucar.edu/Data/BVOC/>
- Nemitz, E., P. Misztal, B. Langford, D. Oram, G. Phillips, C. di Marco, B. Davison, N. Hewitt, N. Cape. 2008. Fluxes and in-canopy gradients of biogenic volatile organic compounds above contrasting South East Asian land uses. EOS Trans AGU 89(53) Fall Meeting Supp.
- Pereira, P.A., L.M.B Santos, E.T. Sousa, J.B. de Andrade. 2004. Alcohol- and Gasohol-Fuels: A Comparative Chamber Study of Photochemical Ozone Formation. *J Braz Chem Soc* 15: 646.
- Peterson, C. and D. Reece. 1996. Emissions characteristics of ethyl and methyl ester of rapeseed oil compared with low sulfur diesel control fuel in a chassis dynamometer test of a pickup truck. *Trans ASAE* 39(3): 805–816.
- Purves, D.W., J.P. Caspersen, P.R. Moorcroft, G.C. Hurtt, S.W. Pacala. 2004. Human-induced changes in US biogenic volatile organic compound emissions: evidence from long-term forest inventory data. *Global Change Bio* 10: 1737–1755.
- Royal Society, The. 2008. Sustainable biofuels: prospects and challenges. Policy document 01/08. Royal Society, London.
- Searchinger, T., R. Heimlich, R.A. Houghton, F.X. Dong, A. Elobeid, J. Fabiosa, S. Tokgoz, D. Hayes, T.H. Yu. 2008. Use of US croplands for biofuels increases greenhouse gases through emissions from land-use change. *Science* 319(5867): 1238–1240.
- SenterNovum. 2008. Participative LCA on Biofuels. Rapport 2GAVE-05,08. Commissioned by VROM. Senternovem GAVE Programme, The Hague NL.
- Sillman, S. and D. He. 2002. Some theoretical results concerning O₃-NO_x-VOC chemistry and NO_x-VOC indicators. *J Geophys Res* 107(D22): 4659.
- Steiner, A., L. Chao, Y. Huang and W.L. Chameides, 2002) Past and present-day biogenic volatile organic compound emissions in East Asia. *Atmos Environ* 36(31): 4895–4905.
- Stohl, A., E. Williams, G. Wotawa, H. Kromp-Kolb. 1996. A European inventory of soil nitric oxide emissions and the effect of these emissions on the photochemical formation of ozone. *Atmos Environ* 30(22): 3741–3755.

- Tanner, R. L., A.H. Miguel, J.B. de Andrade, J.S. Gaffney, G.E. Streit. 1988. Atmospheric chemistry of aldehydes - enhanced peroxyacetyl nitrate formation from ethanol-fueled vehicular emissions. *Environ Sci Techn* 22: 1026-1034.
- Turrio-Baldassarri, L., C.L. Battistelli, L. Conti, R. Crebelli, B. de Berardis, A.L. Iamiceli, M. Gambino, S. Iannaccone. 2004. Emission comparison of urban bus engine fueled with diesel oil and biodiesel blend. *Sci Tot Environ* 327: 147-162.
- Unnasch, S. and M. Chan. 2007. Full fuel cycle assessment: tank-to-wheels emissions and energy consumption. DRAFT report prepared for California Energy Commission. TIAX LLC., Cupertino CA USA
- Wang, M. 2007. "GREET" (Argonne National Laboratory, Argonne, IL, ANL/ESD/05-03. Argonne IL USA.
- Wiedinmyer, C., X. Tie, A. Guenther, R. Neilson, C. Granier. 2006. Future changes in biogenic isoprene emissions: how might they affect regional and global atmospheric chemistry? *Earth Interactions* 10: ARTN 3.
- Wisconsin Department of Natural Resources. 2005. Ozone Air Quality Effects of a 10% Ethanol Blended Gasoline in Wisconsin. DNR Bureau of Air Management, Madison WI, USA.
- WHO (World Health Organization). 2009. Global burden of disease due to indoor air pollution. http://www.who.int/indoorair/health_impacts/burden_global/en/
- Yevich, R. and J.A. Logan. 2003. An assessment of biofuel use and burning of agricultural waste in the developing world. *Glob Biogeochem Cycles* 17(4): 1095
- Young, A.L. 2009. Finding the balance between food and biofuels. *Environ Sci Pollution Res* 16(2): 117-119.