Air pollution impacts of biofuels

KRISTINA WAGSTROM
University of Minnesota, Minneapolis, USA

JASON HILL
University of Minnesota, St. Paul, USA

Abstract
This chapter reviews the impacts of increased liquid transportation biofuel production and use on air pollutant emissions and their ambient concentrations, with a focus on developing nations. Major pollutants covered include those affecting climate change (carbon dioxide, nitrous oxide, and methane) and those affecting human health (carbon monoxide, sulfur dioxide, particulate matter, ammonia, nitrogen oxides, ozone, and volatile organic compounds). Emissions and resulting ambient concentrations associated with all the stages of the full life cycle of biofuel production and use are described and, where possible, are compared against conventional fuels.

Keywords: atmospheric pollution, greenhouse gas emissions, life cycle assessment

1. Introduction
Petroleum is the most commonly used feedstock for producing transportation fuels because it is both convenient and energy dense. Through the years, petroleum has fueled global economic growth, yet it comes at the price of global conflict, exploitation of indigenous peoples, and destruction of both terrestrial and aquatic habitats. In addition, the extraction, refining, and combustion of petroleum is responsible for the emission of many air pollutants that contribute to anthropogenic climate change, harm human health, and damage ecosystems worldwide (Uherek et al., 2010).

Recently, interest has flourished in the use of biofuels as a petroleum replacement (see Chapter 1). Domestically produced biofuels have the potential to support rural communities, slow the depletion of fossil fuel resources, and avoid many of the negative environmental consequences associated with petroleum such as oil spills (Lovett et al., 2011). Similarly, biofuels may reduce greenhouse gas emissions and yield improvements to air quality if the emissions from a biofuel’s production and use
are lower than those associated with meeting the same energy need with conventional fuels.

In reality, whether biofuels are indeed an environmentally preferable choice over conventional fuels is not well understood. What has emerged from the literature is a complex series of trade-offs related to energy security, food supply, ecosystem maintenance, water quality, and air pollution (Gasparatos et al., 2011). Overall, whether a biofuel offers a benefit over the conventional fuel it displaces depends on where and how each fuel is produced and used and what technologies are employed in mitigating their negative effects. To account fully for emissions from biofuel production and use, it is as important to consider those related to feedstock cultivation and harvesting as it is those related to conversion and fuel use. The emissions associated with feedstock cultivation and harvesting depend on both the biofuel feedstock and agricultural practices used. The net impact of increased biofuel production will depend on how and where the global industry develops. If done well, biofuels could help alleviate many of the environmental problems associated with petroleum, but if produced without regard to their potential consequences, they could both exacerbate existing problems and create new ones (Buyx and Tait, 2011; Tilman et al., 2009).

This chapter focuses on one aspect of the many potential trade-offs associated with transitioning to increased biofuel production and use, namely, biofuels’ impact on atmospheric pollutant emissions and their ambient air concentrations. The potential changes in various pollutant emissions and ambient concentrations are discussed, including how they contribute to climate change and how they affect human health. Special attention is given to developing nations. Where possible, comparisons between biofuel options and current conventional fuels are presented from a life cycle perspective, as air pollutant emissions may occur throughout all stages of fuel production and use. This chapter is meant to serve as a reference list of major air pollutant species considered in the recent biofuel-focused literature, but not all air pollutants and their effects are covered.

2. Overview of atmospheric pollutants

As a starting point for understanding the impacts of biofuels on air pollution levels, it is important to understand the pertinent atmospheric pollutants that relate to gasoline and liquid biofuel production and use. Pollutants are often classified by the major risks associated with them, primarily climate change potential and negative human health impacts. In addition to these risks, there are also potential risks associated with crop damage, ecosystem destruction, and visibility deterioration.

The major greenhouse gas species of concern when considering biofuels are carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O), of which the effects on human health and well-being via climate change are well described (Confalonieri et al., 2007; Tol, 2009). The pertinent species that are known to impact human
respiratory and cardiopulmonary systems are carbon monoxide (CO), sulfur dioxide (SO\textsubscript{2}), particulate matter (PM),\textsuperscript{1} ammonia (NH\textsubscript{3}), nitrogen oxides (NO\textsubscript{x}), and ozone (O\textsubscript{3}). In addition, there is also concern with changes in volatile organic compound (VOC) concentrations because they are an integral contributor to the formation of ozone and some forms of PM in the atmosphere (Seinfeld and Pandis, 2006). Other serious health impacts arise directly from emissions of two classes of VOCs, carbonyls and aromatics, of which many species are known to have carcinogenic properties.

In addition to risk classification, pollutants are also classified as either primary or secondary species. Primary pollutants are emitted directly into the atmosphere from either anthropogenic (human) or biogenic (natural) sources. The relationship between emissions changes and the resulting ambient concentration changes are often more easily understood for these pollutants as a decrease in emission rates typically translates into a decrease in ambient concentrations. Secondary pollutants are formed in the atmosphere via chemical reactions or physical processes. The concentration response to changes in emissions for these species is often more difficult to predict as the chemical and physical processes that impact their concentrations are often highly dependent on meteorology (e.g., relative humidity and temperature) and the relative concentrations of the precursor species (i.e., the species that react to form the species of interest) (Seinfeld and Pandis, 2006). Species can be both primary and secondary if they are both directly emitted and formed in the atmosphere, such as with PM.

Studies investigating the potential changes in air pollution associated with the production and use of biofuels in place of conventional fuels are becoming increasingly important for policy makers and regulators. Much of the initial work done in this area was focused on quantifying changes in emission rates from vehicles fueled by biofuel mixtures compared to gasoline, but more recent work has recognized the importance of identifying emissions associated with the whole fuel life cycle. For example, for ethanol from corn grain in the United States, the fuel-use phase, which includes tailpipe emissions and evaporative emissions from vehicles and filling stations, is responsible for over 90 percent of life cycle CO emissions but only 68 percent of VOCs, 22 percent of primary PM\textsubscript{2.5} (PM with diameters less than 2.5 \textmu m), 17 percent of NO\textsubscript{x}, 13 percent of NH\textsubscript{3}, and \textless 1 percent of SO\textsubscript{2} emissions (Figure 3.1). Table 3.1 provides a brief summary of the different pollutants covered in this chapter and their risks, main sources, and general trends associated with increased biofuel use.

### 2.1. Greenhouse gases

Greenhouse gases (GHG) are the atmospheric trace gases that absorb incoming infrared radiation and provide warmth to the atmospheric surface. As their concentrations change, so does the amount of radiation that is being absorbed, therefore

\textsuperscript{1} PM also contributes to climate change; refer to Section 2.4.
### Table 3.1. Brief summary of the different pollutants emitted during biofuel production and use

<table>
<thead>
<tr>
<th>Pollutant species</th>
<th>Primary risk</th>
<th>Major contributing processes</th>
<th>Trends found in literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenhouse gases (CO₂, N₂O, CH₄)</td>
<td>Climate change</td>
<td>Land use change, fossil fuel use in farming and biofuel production, fertilizer production and use</td>
<td>Life cycle emissions highly depend on feedstock, production technology, and any associated land use change</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td>Health concerns</td>
<td>Vehicular combustion, agricultural burning</td>
<td>Most studies find decreases in tailpipe emissions and increases from agricultural burning</td>
</tr>
<tr>
<td>Sulfur dioxide (SO₂)</td>
<td>Respiratory concerns, acid rain</td>
<td>Electricity-generating facilities, phosphate fertilizer production</td>
<td>Largest changes are expected from the change in electricity demand for fuel processing and are process dependent</td>
</tr>
<tr>
<td>Particulate matter (PM)</td>
<td>Respiratory and cardiopulmonary concerns, ecosystem damage, visibility deterioration, building damage</td>
<td>Farming, fuel processing, fertilizer production</td>
<td>Potential increases in rural areas; major changes expected from the change in electricity demand for fuel processing</td>
</tr>
<tr>
<td>Ammonia (NH₃)</td>
<td>Formation of secondary particulate matter</td>
<td>Fertilizer use, catalytic converters in vehicles</td>
<td>Likely increases with increases in fertilizer needs</td>
</tr>
<tr>
<td>Nitrogen oxides (NOₓ)</td>
<td>Respiratory concerns, ozone formation</td>
<td>Vehicular combustion, fuel processing, farming and land use change, fertilizer production</td>
<td>Found increases in rural areas and decreases in urban areas</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>Respiratory concerns, decrease in crop yields</td>
<td>Chemical formation in the atmosphere</td>
<td>The results are varied, but most life cycle assessments indicate an increase in ozone concentrations with ethanol use</td>
</tr>
<tr>
<td>Volatile organic compounds (VOCs)</td>
<td>Carcinogenicity, ozone formation</td>
<td>Vehicular combustion, evaporative emissions, biogenic emissions</td>
<td>Found decreases in benzene and 1,3-butadiene emissions and increases in formaldehyde and acetaldehyde emissions</td>
</tr>
</tbody>
</table>
leading to changes in atmospheric temperature. The main GHGs that are of importance when discussing biofuels are carbon dioxide (CO$_2$), nitrous oxide (N$_2$O), and methane (CH$_4$).

The carbon released as CO$_2$ on burning biofuels is the same carbon fixed by plants during photosynthesis. In life cycle carbon accounting of biofuels, therefore, tailpipe emissions of CO$_2$ are completely offset by atmospheric reductions in CO$_2$ from plant growth. Only trace amounts of N$_2$O and CH$_4$ are emitted on biofuel combustion. For biofuels, the focus of GHG accounting is therefore not on emissions in use but rather on both emissions in production and market-mediated effects. GHG emissions in biofuel production include those from agricultural activities, transport of feedstocks, biorefinery processes, biofuel distribution, and any supporting upstream activities. GHG emissions due to market-mediated effects include those that result from direct
and indirect land use changes caused by the conversion of former food-producing croplands or native vegetation for feedstock production.

A wealth of studies exists that have estimated life cycle GHG emissions from food, animal feed, and lignocellulosic-based biofuels. These studies have been reviewed in more than a few instances (Bessou et al., 2010; Fargione et al., 2010; Hoefnagels et al., 2010; Kendall and Chang, 2009; Liska and Cassman, 2008; Sims et al., 2010; van der Voet et al., 2010). Overall trends in the climate change impacts of biofuels can be gleaned from these studies. An important caveat when interpreting biofuel GHG accounting studies is that a wide range of methodologies exist and that differences in results are, essentially, as likely to be due to the different methodologies being employed as to the different biofuel production pathways being considered (Anderson-Teixeira et al., 2011; Stratton et al., 2011; Wang et al., 2011).

The choice of feedstock crop has a large impact on the anticipated life cycle of GHG emissions as the CO$_2$ fluxes associated with tillage and N$_2$O fluxes associated with nitrogen fertilizer use are potentially large sources of GHG emissions. Biofuels produced from perennial crops (e.g., switchgrass, miscanthus), which are not tilled annually and typically use nitrogen more efficiently, tend to have lower GHG emissions than those from annual crops (e.g., corn). Biofuels produced in biorefineries that use natural gas to provide heat tend to have lower GHG emissions than biorefineries that use coal (Wang et al., 2011). The use of biomass for process heat in biorefineries tends to lead to even lower emissions. EPA (2009) found that the GHG emissions associated with fuel production varied widely and could even have cobenefits such as the displacement of current power plant emissions by excess electricity that is fed back into the grid. Methane (CH$_4$) is of interest because it is potentially emitted when used as a heat source for different process steps and because it serves as a material feedstock for nitrogen fertilizer production (Montzka et al., 2011).

Because of the potential for large GHG emissions associated with land use change (Fargione et al., 2008; Gibbs et al., 2008; Hertel et al., 2010; Searchinger et al., 2008), there is large uncertainty about whether food and animal feed–based biofuels such as corn grain ethanol and soybean biodiesel reduce GHG emissions relative to petroleum-derived fuels (Mullins et al., 2011; Plevin et al., 2010) (refer to Chapters 6 and 13). Many recent studies have evaluated GHG emissions associated with the life cycle of lignocellulosic biofuels and have found considerable potential for significant reductions with a variety of different feedstocks. In general, biofuels produced from wastes and residues are more likely to have GHG emissions lower than biofuels produced from dedicated bioenergy crops due to uncertainties associated with GHG emissions from land use change (Spatari and MacLean, 2010).

### 2.2. Carbon monoxide

Carbon monoxide (CO) is a gaseous species that is mainly present in the atmosphere as a result of incomplete combustion and, to a lesser extent, oxidation of larger organic

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species in the atmosphere (Finlayson-Pitts and Pitts, 2000). Vehicular combustion processes are high contributors to CO emissions because incomplete combustion is more common in vehicles than in larger stationary combustion sources such as power plants. CO is a concern to human health because it reduces the ability of hemoglobin to transport oxygen. Levels of CO found in ambient air in much of the world are of little concern to the majority of the population, but elevated ambient levels can be dangerous for individuals with preexisting heart conditions or to those in areas of the world with higher ambient CO concentrations (Jacobson, 2002).

Many studies have measured emission rates of CO from engines run on various blends of biofuels and conventional fuels. As E10 (a blend of 10% ethanol and 90% gasoline) is often employed during the winter in the northern United States to maintain lower ambient CO levels, it is not surprising that in many studies, the addition of small amounts of ethanol as an oxygenate to gasoline has been shown to decrease CO emissions (EPA, 2007). Studies aimed at determining the changes in CO emissions for higher ethanol blends from a variety of vehicles and under a variety of operating conditions have found mixed results. Kelly et al. (1996) found that E85 decreased CO emissions by 12 to 24 percent, while Jacobson (2007) found a slight increase (5%) in CO emissions from E85 combustion. In addition, Graham et al. (2008) conducted a statistical analysis of the relevant results available in literature and found a 16 percent reduction in CO emissions for E10 blends but no significant change in CO emissions for E85 blends. For biodiesel blends, researchers have seen significant reductions in CO emissions during vehicular operation (McCormick, 2007), even as high as a 50 percent reduction for B100 (100% biodiesel) (EPA, 2002).

Studies that look beyond the tailpipe to include full life cycle emissions for CO have also found mixed results. The majority of these studies show an increase in the prepump CO emissions for ethanol, whether from corn grain or cellulosic feedstocks, and, as described earlier, a decrease in fuel usage emissions compared to gasoline (Hess et al., 2009; Huo et al., 2009). Hess et al. (2009) found that when agricultural burning was accounted for in the life cycle emissions for sugarcane feedstocks, ethanol use led to a several-fold increase in CO emissions compared to emissions from the gasoline life cycle. This is an important consideration in countries where burning is common agricultural practice (e.g., Brazil; refer to Chapter 6) or is associated with land clearing for increased demand for cropland (e.g., Indonesia; refer to Chapter 9). Sheehan et al. (2004) found increases in CO when considering the full life cycle of using ethanol from corn stover in the midwestern United States. Similar studies for biodiesel have largely shown an increase in CO emissions for a full life cycle analysis of biodiesel over traditional diesel (Delucchi, 2006).

### 2.3. Sulfur dioxide

Sulfur dioxide (SO\textsubscript{2}) is a primary gaseous pollutant – over 70 percent of its emissions in the United States come from fossil fuel–powered electricity-generating facilities.
SO$_2$ can cause respiratory irritation when inhaled as it can dissolve in the moist air of the respiratory system to form an acidic solution. In addition, SO$_2$, or its oxidation product, sulfuric acid, can dissolve in cloud droplets to form an acidic solution resulting in acid rain. Acid rain can have devastating impacts on sensitive ecosystems both through immediate impacts of the dilute acid solution coming into contact with surfaces of leaves and through the accumulation of acid in soils and bodies of water over time (Jacobson, 2002). Oxidation of SO$_2$ and subsequent condensation of the oxidation product is also the major source of the sulfate that is found in particulate matter.

Both ethanol and biodiesel contain little to no sulfur, so it is expected that tailpipe emissions of SO$_2$ will be lower for vehicles fueled with biofuels than for those fueled with gasoline and conventional diesel. As vehicular SO$_2$ emissions are quite small compared to those from electricity-generating facilities, this will likely not have a large impact on SO$_2$ concentrations in the atmosphere. Hess et al. (2009) hypothesized that benefits in SO$_2$ reduction from displacing conventional fuels with biofuels might be more pronounced in countries with higher sulfur contents in liquid fuels. More likely, the most significant changes in SO$_2$ emissions due to biofuel use will occur as part of the fuel production stage, considering that the energy requirements to process each different fuel and biofuel feedstock are different. Hess et al. (2009) found that life cycle emissions of E85 produced from cellulosic feedstock, specifically corn stover and sugarcane, resulted in a decrease in SO$_2$ emissions compared to those from gasoline, while E85 produced from corn grain resulted in an increase in SO$_2$ emissions. In some studies, cellulosic E85 even resulted in a decrease in overall SO$_2$ emissions from the baseline value as excess electricity, produced as a coproduct from the ethanol plant, would be fed back into the grid and displace SO$_2$ from coal-fired power plants (Spatari et al., 2010). These impacts will likely be strongest in areas with high fractions of electricity production supplied by coal, including China, India, and South Africa. Carrying out a full life cycle assessment, Sheehan et al. (2004) found increases in SO$_2$ emissions in the midwestern United States for corn stover ethanol use, and Rettenmaier et al. (2010) found increases in SO$_2$ emissions for sugar beet ethanol in Europe.

### 2.4. Particulate matter

Atmospheric PM is a collection of fine particles suspended in air ranging in size from 1 nm to as large as 100 µm. They are emitted from natural sources, such as sea salt and dust, or from anthropogenic sources, such as diesel trucks and power plants. PM has a complicated composition as it is comprised of a variety of different chemical species. Primary PM is emitted directly into the atmosphere from a variety of sources, with combustion being a large contributor in many areas, particularly in developing nations. Secondary PM can be formed in the atmosphere when gaseous species with
low volatilities are able to condense onto preexisting PM. These gaseous species can either be those that are directly emitted (e.g., ammonia condenses to form ammonium salts) or oxidized versions of gaseous primary species (e.g., SO$_2$ is oxidized to form sulfuric acid and condenses to form sulfate salts). Many organic species also undergo oxidation reactions that lower their volatilities and may condense to form additional PM.

Dozens of studies have found positive correlations between PM concentrations and mortality and hospital admission rates for respiratory illness and heart disease (Dockery et al., 1993; Klemm et al., 2000). Other significant impacts of increased PM concentrations include decreases in visibility (Pilinis, 1989), damage to buildings (Esbert et al., 2001; Marinoni et al., 2003), and ecosystem damage (Seinfeld and Pandis, 2006).

In addition to its health impacts, PM also affects climate change. PM can directly impact the radiative balance of Earth by absorbing incoming and outgoing radiation (particularly black carbon) or reflecting incoming radiation back out of the atmosphere (the aerosol direct effect). PM can also impact the radiative balance by changing the lifetime and radiative balance of clouds (the aerosol indirect effect). Both impacts are complex and can potentially have a warming impact in some locations and a cooling impact in others (Forster et al., 2007).

Biodiesel has been found to have lower PM tailpipe emissions than conventional diesel (EPA, 2002). For ethanol fuel blends, there has been little research on changes in tailpipe PM emissions as the PM emissions from both gasoline and ethanol are low (EPA, 2007). Lara et al. (2005) utilized principal component analysis to study PM concentrations near the Brazilian city of Piracicaba to show that 60 percent of the PM found during the study was attributable to burning of sugarcane fields and that an additional 14 percent was related to soil dust, primarily from agricultural practices (refer to Chapter 6). They also found significant increases in black carbon concentrations during the burning season, which can have implications for climate change. Allen et al. (2004a), also studying high sugarcane-producing areas of Brazil, observed peak PM concentrations up to 240 $\mu$g/m$^3$ during the burning season. The implications of these abnormally high concentrations can be seen in studies that have shown increases in hospital admissions during the agricultural burning season in these regions (Arbex et al., 2010), particularly among the young and elderly (Cançado et al., 2006). These findings have significant ramifications for PM concentrations in areas of South America, Africa, and Asia that still practice agricultural burning. Studying the life cycle emissions from ethanol production in India, Kadam (2002) found that using bagasse-derived ethanol as a fuel additive may result in a decrease in PM emissions.

Hill et al. (2009) investigated the life cycle PM concentrations expected from ethanol use in the United States with a variety of ethanol feedstocks. They found that when compared to life cycle emissions from gasoline, corn grain ethanol resulted in a significant increase in PM emissions, while cellulosic feedstocks (corn stover,
miscanthus, mixed prairie plant species, and switchgrass) led to PM emission decreases. Kusiima and Powers (2010) calculated the anticipated societal costs associated with a variety of fuel sources and found high PM costs associated with ethanol, with the majority of the PM emissions associated with fuel processing, farming, and fertilizer production (these results were not compared to those for gasoline). Finally, Huo et al. (2009) also found increases in PM emissions for corn grain ethanol in place of gasoline but noted that the main PM increases were in rural areas and anticipated decreases were in many urban areas.

2.5. Ammonia

Ammonia (NH$_3$) is a basic gaseous pollutant primarily emitted from animal waste, the breakdown of organic materials, fertilizer production and use, and industrial processes (Seinfeld and Pandis, 2006). The main risk associated with ammonia in the atmosphere is the role it plays in the formation of secondary PM. Ammonia neutralizes sulfuric and nitric acids to form ammonium sulfate and ammonium nitrate salts that condense to form PM.

The main ammonia source associated with biofuels is ammonia volatilization from nitrogen fertilizers applied to croplands to grow biofuel feedstocks. For this reason, the emission of ammonia associated with biofuels is highly variable by season (Goebes et al., 2003). Emissions of ammonia also depend greatly on the amount and type of fertilizer applied and how efficiently the crop utilizes the nitrogen in the fertilizer (Bouwman et al., 2010). Bouwman et al. (2002) found that globally, 14 percent of the nitrogen applied as synthetic fertilizers and 23 percent of that applied as animal manure is lost due to volatilization of ammonia. In addition, they found that emissions in developing nations tend to be higher than in industrialized countries due to higher temperatures and the higher use of urea and ammonium salts. They found 18 percent and 7 percent volatilization of ammonia in developing and industrialized countries, respectively, for synthetic fertilizer and 26 percent and 21 percent, respectively, for animal manure. Because some crops use nitrogen in fertilizers more efficiently and require less fertilizer application, the type of crop that is being grown can have a large impact on the ammonia emissions (Miller et al., 2006). Another important factor in ammonia volatilization is the technique that is used to apply the fertilizer to the soil, though different application methods can result in more ammonia runoff into groundwater (Aneja et al., 2009).

Another source of ammonia emissions is vehicle tailpipes (Durbin et al., 2004; Kean et al., 2000), although this is a minor source compared to nitrogen fertilizer production and use. These emissions are the result of a reaction on the surface of the three-way catalytic converter. Unlike most pollutants, ammonia emissions increased during the initial implementation of three-way catalytic converters but have started to decline again in recent vehicle models (Burgard et al., 2006).
2. Overview of atmospheric pollutants

2.6. Nitrogen oxide

The term NO$_x$ refers to a variety of nitrogen oxide species that exist in the atmosphere. The two primary contributing species to NO$_x$ concentrations are nitrogen monoxide (NO) and nitrogen dioxide (NO$_2$). NO$_2$ has been shown to cause airway inflammation in individuals exposed to high concentrations (Jacobson, 2002). High NO$_x$ concentrations tend to be most prevalent near roadways as vehicular sources are the main contributors. In addition to its direct impacts, NO$_x$ plays an important role in ozone formation. This role is highly nonlinear, meaning that lowering NO$_x$ concentrations may increase, decrease, or have no effect whatsoever on ozone levels in certain areas. The relative composition of the atmosphere, particularly the ratio between NO$_x$ and VOC concentrations, plays an important role in determining which of the end results mentioned earlier will actually occur (Finlayson-Pitts and Pitts, 2000). Finally, NO$_x$ can also be oxidized in the atmosphere to form nitric acid, which will potentially condense on PM to form nitrate salts and can also contribute to acid rain (Seinfeld and Pandis, 2006).

Many studies have found increases in NO$_x$ emissions from increased proportions of biodiesel in blended fuels (EPA, 2002; McCormick, 2007; Morris et al., 2003). The results from studies investigating NO$_x$ emissions from different biofuel blends have been varied. In a survey of the literature, Yanowitz and McCormick (2009) found that the use of E85 reduced emissions of NO$_x$ by 54 percent on average, but individual studies, such as that of the National Renewable Energy Laboratory (NREL, 1999), have found that emissions of NO$_x$ increased by 33 percent. Many additional studies have also found values within this range. Much of this variability is likely related to differences in testing procedures, including engine load, vehicle type, and operating temperature, all of which potentially have a large impact on the levels of emitted pollutants, particularly of NO$_x$ and CO. In a similar literature review, Graham et al. (2008) found that on average, NO$_x$ emissions decreased by 45 percent with E85 but remained unchanged with E10 blends.

Studies that have considered NO$_x$ emissions throughout the biofuel life cycle have found that NO$_x$ emissions associated with farming, fuel processing, and fertilizer production could potentially outweigh any potential NO$_x$ emissions decrease associated with biofuel use (Hess et al., 2009; Hu et al., 2004). Martinelli and Filoso (2008) estimate high NO$_x$ emissions from the approximately 4.9 million ha of sugarcane fields in Brazil that still utilize burning. These emissions could contribute to the high nitric acid content of rainwater in the area (Lara et al., 2001). There is also concern that next-generation biorefineries may emit high levels of NO$_x$. On a per volume basis, NO$_x$ emissions from lignocellulosic ethanol demonstration facilities are approximately an order of magnitude higher than currently observed emissions from commercial corn grain ethanol facilities and petroleum refineries (Jones, 2010). Kusiima and Powers (2010) found that NO$_x$ emissions from fertilizer production, farming, and processing
were the main contributors to the societal costs associated with ethanol. As much of the fertilizer used globally is produced in developing nations, these emissions have the potential to affect air pollutant concentrations in those areas. Huo et al. (2009) found increases in NO\textsubscript{x} concentrations in rural areas but decreases in urban areas. As many rural areas are NO\textsubscript{x} limited, these increases could very well lead to increases in localized ozone concentrations, but as the ozone concentrations in these areas are often already relatively low and there are fewer people to be exposed, the net impact on human health may be less severe.

A large set of unknowns related to the air pollution impacts of biofuel production comes from the potential changes in NO\textsubscript{x} emissions due to land use change. It is likely that land use changes will have particularly large impacts in regions where rainforests and peat swamps could be potentially converted to croplands to meet additional demand. Hewitt et al. (2009) investigated the potential for increases in NO\textsubscript{x} emissions in Thailand where native rainforests are replaced with oil palm plantations, and found potential increases in NO\textsubscript{x} emissions that would likely lead to increased O\textsubscript{3} concentrations as these palm plantations are also large sources of VOCs.

2.7. Ozone

Reducing ambient ground-level ozone (O\textsubscript{3}) concentrations is a complicated process for several reasons. Ground-level ozone is not emitted directly but is instead formed via a series of chemical reactions involving two chemical precursors, NO\textsubscript{x} and VOCs, in the presence of sunlight. The chemical reactions that generate ozone are complex and interdependent. Lowering emissions of a precursor will not necessarily yield an improvement in ozone concentrations and depends strongly on the relative abundance of the two precursors (NO\textsubscript{x}; VOCs) as well as on local conditions such as temperature (NRC, 1999). In some cases, emission reductions can actually increase ozone concentrations. Existing research shows that in areas with an abundance of VOCs (NO\textsubscript{x}-limited regimes), reducing NO\textsubscript{x} improves ozone but reducing VOCs has little impact. In areas with an abundance of NO\textsubscript{x} (VOC-limited regimes), reducing VOCs improves ozone but reducing NO\textsubscript{x} often actually increases ozone concentrations, including the peak ozone concentrations regulated by many governments. This non-linearity is the result of competing reactions at higher NO\textsubscript{x} concentrations (Seinfeld and Pandis, 2006). VOC-limited regimes typically exist in urban and suburban areas, whereas NO\textsubscript{x}-limited regimes typically exist in more rural areas.

Ozone exposure increases susceptibility to respiratory infections, medication use by asthmatics, and hospital admissions for individuals with respiratory disease (Halonen et al., 2010). Ozone may also contribute to premature death (Bell et al., 2006; Jerrett et al., 2009), reduced crop yields, and harm to sensitive ecosystems (Van Dingenen et al., 2009).

Of the pollutants that cause the greatest concern, should an increase in biofuel use occur, ozone is the most complex. For the reasons explained earlier, it is difficult
to determine potential changes in ozone concentrations from changes in pollutant emissions. For this reason, it is necessary to incorporate some form of air quality modeling into any study focused on potential ozone concentration changes. Like many other pollutants, studies related to changes in ozone concentrations associated with increased biofuel production and use show mixed results. Luo et al. (2009) found no significant increase in photochemical oxidation potential – a metric related to ozone production – expected from a life cycle analysis of sugarcane-derived ethanol, while the U.S. Environmental Protection Agency (EPA, 2007) found maximum ozone concentration increases (up to 0.33 ppb) with an average increase of 0.153 ppb over the entire United States in high-ethanol-use areas for corn grain ethanol. Jacobson (2007) found increases of over 2 ppb in the Los Angeles area, accounting for changes in tailpipe emissions that could lead to a 9 percent increase in ozone-related mortality, hospitalization visits, and asthma in the region. This reiterates that even though a 2 ppb increase seems relatively small compared to the 75 ppb U.S. National Ambient Air Quality Standard, it may still have a significant impact on human health. In addition, Cook et al. (2010) found increases of up to 1 ppb when investigating increases in biofuel use in the United States. The findings were highly spatially dependent and found ozone decreases in a few highly populated areas. Alhajeri et al. (2011) found modeled changes in maximum ozone concentrations ranging from $-2.1$ to $2.8$ ppb when modeling the impacts associated with replacing gasoline with E85 in Austin, Texas.

In studies that have modeled potential changes of ozone in urban areas, including the study by Jacobson (2007), very large increases in ozone concentrations have been predicted. For instance, Milt et al. (2009) predicted maximum increases of up to 16 ppb in peak ozone concentrations with the replacement of gasoline and diesel with E10 and B10, respectively, in Bangkok, Thailand. Ginnebaugh et al. (2010) found increases of 7 ppb in ozone in the summer and 39 ppb in the winter in southern California. These high predicted increases are likely the result of the low mixing rates between the modeled domain and the surrounding atmosphere coupled with the high acetaldehyde and formaldehyde emissions associated with ethanol fuel usage.

Most studies on biofuels and ozone have focused on locations within the United States. Future research in other areas of the world would shed light on the complexity of ozone formation and its impacts as a result of biofuel production and use. For example, based on studies of Thailand oil palm plantations, land use change may well lead to increases in ozone in some areas (Hewitt et al., 2009).

### 2.8. Volatile organic compounds

Hundreds of species fall into the category of VOCs. These species have a variety of properties, and many of them play an integral role in ozone formation. Sources of VOC species are as varied as the species themselves. However, the most important
biofuel-related sources are evaporative emissions from vehicles, incomplete combustion emissions from vehicles, and biogenic emissions from plants.

The impacts of VOCs are threefold. First, many are harmful to human health as they are carcinogenic. Second, they contribute to the formation of ground-level ozone. Third, many can be oxidized and condense on preexisting PM to create secondary organic aerosols that are also associated with serious health impacts. This section discusses the changes in the total emissions of these species as they relate to increased ozone formation potential. As measuring and reporting these species individually can often be unrealistic, there are three common ways VOCs are grouped and measured for emissions purposes: nonmethane hydrocarbons (NMHC), nonmethane organic gases (NMOG), and total organic gases (TOG). NMHCs include all organic gases comprised of only carbon and hydrogen, whereas NMOGs contain all organic gases except methane. TOGs comprise NMOGs and methane.

Results from studies investigating differences in VOC emissions from biofuels and conventional fuels are mixed. Many studies indicate that higher biofuel blends, including both ethanol and biodiesel, lead to decreases in NMHC emissions from vehicular use (Graham et al., 2008; Kelly et al., 1996; Yanowitz and McCormick, 2009) but also indicate increases of NMOG emissions as these include ethanol and carbonyl emissions from incomplete combustion (Jacobson, 2007). Increases of NMOG emissions of up to 63 percent have been found in tailpipe emission studies in which E85 was used in place of gasoline (Winebrake et al., 2001). NMOG emissions have been found to increase with increasing fuel ethanol content (Durbin et al., 2007). These species can have important impacts on $O_3$ concentrations and are of great importance when considering changes in air quality from the use of biofuels. It is also expected that VOC emissions will change significantly in response to land use change, particularly in areas where rainforests or peat swamps could potentially be converted to croplands. For instance, Hewitt et al. (2009) found that palm trees grown on plantations in Thailand have higher VOC emissions than the native rainforest they replaced. This increase in VOCs along with the potential increase in soil NO$_x$ emissions from increased fertilizer use could lead to substantial increases in ozone concentrations in these areas. Conversely, Eller et al. (2011) demonstrated that growing switchgrass may have lower VOC emissions than those expected from growing other feedstocks. More research is needed to understand VOC emissions from the cultivation of different biofuel feedstocks.

Four chemical species are of particular interest when discussing VOC emissions from biofuels. These species have both carcinogenic properties and strong ozone formation potential. They are, in order of decreasing Cancer Unit Risk Estimate, as defined by the EPA, 1,3-butadiene, formaldehyde, benzene, and acetaldehyde (Jacobson, 2007). Most studies related to the changes in these emissions focus on laboratory tests of vehicles running on different fuels and fuel blends. These tests indicate that high ethanol fuel blends, such as E85, are expected to produce benzene emissions
that are approximately 60 to 85 percent lower than those from gasoline (Black et al., 1998; Graham et al., 2008; Kelly et al., 1996; Winebrake et al., 2001). Emissions of 1,3-butadiene have also been shown to decrease by 70 to 80 percent with higher ethanol blends (Graham et al., 2008; Kelly et al., 1996; Winebrake et al., 2001).

Unlike benzene and 1,3-butadiene emissions, a shift from gasoline to E85 blends could increase formaldehyde emissions by 20 percent (Kelly et al., 1996) to 315 percent (Winebrake et al., 2001). Acetaldehyde emissions are predicted to increase by over 10 times the current vehicular emission levels (Graham et al., 2008; Jacobson, 2007; Kelly et al., 1996; Winebrake et al., 2001). Some studies have found increases in acetaldehyde emissions in excess of 3,000 percent (Black et al., 1998; Magnusson et al., 2002). These results have been found to align with measurements of formaldehyde and acetaldehyde concentrations in Brazil, where ethanol use is high, as the ambient concentrations of acetaldehyde and formaldehyde are higher than in the rest of the world and the concentrations of aromatics such as benzene are lower than in much of the world (Anderson, 2009; Nguyen et al., 2001). Correa et al. (2003) found particularly high concentrations of formaldehyde (1.5–54.3 ppb) and acetaldehyde (2.4–45.6 ppb) near roadways in Rio de Janeiro, Brazil. Using an air quality model, Jacobson (2007) found increases of over 0.7 ppb and 0.07 ppb for acetaldehyde and formaldehyde, respectively, in a modeling study of E85 use. These increases are particularly significant for acetaldehyde, which had ambient concentrations around 2.5 ppb in this study. These increases are most problematic concerning their ozone formation potential, and Jacobson (2007) did find significant increases in ozone in the same study.

In addition to the studies mentioned earlier, Correa and Arbilla (2008) found biodiesel blends to have increased acetaldehyde, formaldehyde, acrolein, acetone, propionaldehydes, and butyaldehyde emissions and decreased benzaldehyde emissions when compared to emissions from conventional diesel combustion. These species have varied levels of ozone formation potential and associated cancer risks.

Another group of organic species of interest when considering biofuels are polycyclic aromatic hydrocarbons (PAHs). These compounds, like those mentioned previously, are also carcinogenic. Many studies have indicated that PAH concentrations are expected to decrease with increasing biofuel use (de Abrantes et al., 2009; McCormick, 2007; Turrio-Baldassarri et al., 2004). Conversely, Martinelli and Filoso (2008) theorize that high PAHs in certain areas of Brazil are likely attributable to sugarcane burning. Some rural areas have concentrations that are higher than those typically found in large cities.

### 3. Conclusions

Around 90 percent of global biofuel production occurs in the United States and Brazil (Timilsina and Shrestha, 2010; Wiens et al., 2011), and so it is not at all surprising
that few studies on the air pollution impacts of biofuels have focused on developing nations. Much of what has been learned from the United States and Brazil can be used to inform biofuel policies in developing nations, but because of the location- and timing-specific factors described earlier, further insight into the issues associated with growing biofuel production in developing nations will need to be nation specific.

Studies that have investigated the potential air quality impacts of the production and use of biofuels have shown that displacing conventional fuels will likely lead to some localized improvements in air quality. Varied findings are as much the result of the differing experimental setups and modeling approaches used in the studies reviewed in this chapter as they are the result of the differences among the effects of the fuels themselves as they are deployed for vehicular transportation. It is also important to note that studies often do not account for emerging engine and emission control technologies. Many findings related to vehicular emissions for the different pollutants discussed in this chapter have the potential to change dramatically as engines are redesigned to better accommodate new fuels and meet new emission standards (Twigg, 2005). These changes in emissions will likely lead to changes in ambient concentrations. For instance, Correa et al. (2010) found decreases in ambient formaldehyde and acetaldehyde concentrations in Brazil from 2004 to 2009 that were associated with the implementation of new engine technologies.

Any air pollution benefits associated with transitioning from conventional fuels to biofuels may also be augmented through the use of improved agricultural practices, better conversion technologies, and the production of advanced liquid biofuels beyond ethanol and biodiesel. So-called green hydrocarbons derived from lignocellulosic biomass have the potential to be produced with much greater efficiency than the current generation of biofuels (Regalbuto, 2009), which may translate into a reduction of air pollutants across their entire life cycle. Future studies will help increase our understanding of what air quality changes to anticipate as the use of biofuels becomes more prevalent.

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