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A Spatially and Temporally Explicit Life Cycle Inventory of Air Pollutants from Gasoline and Ethanol in the United States

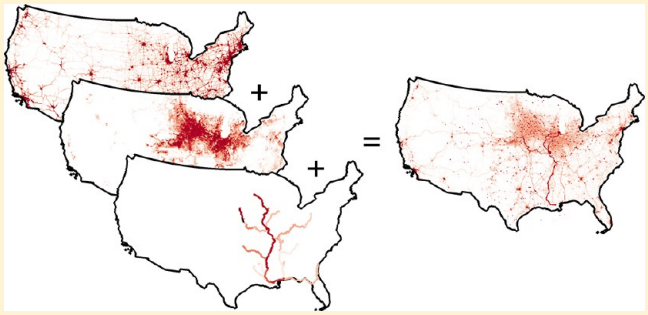
Christopher W. Tessum,[†] Julian D. Marshall,[†] and Jason D. Hill*[,‡]

[†]Department of Civil Engineering, University of Minnesota, Minneapolis, Minnesota, United States

[‡]Department of Bioproducts and Biosystems Engineering, University of Minnesota, St. Paul, Minnesota, United States

Supporting Information

ABSTRACT: The environmental health impacts of transportation depend in part on where and when emissions occur during fuel production and combustion. Here we describe spatially and temporally explicit life cycle inventories (LCI) of air pollutants from gasoline, ethanol derived from corn grain, and ethanol from corn stover. Previous modeling for the U.S. by Argonne National Laboratory (GREET: Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation) suggested that life cycle emissions are generally higher for ethanol from corn grain or corn stover than for gasoline. Our results show that for ethanol, emissions are concentrated in the Midwestern "Corn Belt". We find that life cycle emissions from ethanol exhibit different temporal patterns than from gasoline, reflecting seasonal aspects of farming activities. Enhanced chemical speciation beyond current GREET model capabilities is also described. Life cycle fine particulate matter emissions are higher for ethanol from corn grain than for ethanol from corn stover; for black carbon, the reverse holds. Overall, our results add to existing state-of-the-science transportation fuel LCI by providing spatial and temporal disaggregation and enhanced chemical speciation, thereby offering greater understanding of the impacts of transportation fuels on human health and opening the door to advanced air dispersion modeling of fuel life cycles.



INTRODUCTION

On-road transportation accounts for approximately 20% of United States energy consumption.[1] Associated tailpipe emissions alone account for 40−60% of ground-level ozone (O_3) precursors, 6% of fine particulate matter ($PM_{2.5}$),[2] and 22% of greenhouse gases (GHGs)[3] emitted. Upstream processes involved in fuel production also contribute to overall environmental impacts. Life cycle assessment (LCA) has been used extensively to quantify the combined effects of fuel production and use,[4,5] but descriptions of where and when emissions occur are typically not reported in life cycle inventories (LCI). Such information is generally not relevant for long-lived GHGs or for fossil fuel depletion, which together have received overwhelming attention among extant LCAs of transportation fuels. For many non-GHG pollutants, knowledge of spatial and temporal aspects of emissions is critical for understanding life cycle impacts; such information has been identified as a priority for inclusion in future analyses.[6−8]

Many extant LCAs incorporate spatial and temporal information to some degree (e.g., spatially explicit treatment of a single process within the life cycle,[9−16] country, region, or state-specific impact factors,[17−27] disaggregation by urban versus rural locations,[28] county-specific information for the whole life cycle,[1,29] or spatial and temporal information for aggregated groups of processes.)[30,31] Here we add process-specific spatial and temporal information to an existing attributional life cycle inventory (LCI) so as to reveal patterns in the geographic distribution and intra-annual timing of emissions. We focus on transportation fuels in the U.S. and analyze three fuels pathways: gasoline, ethanol from corn grain, and cellulosic ethanol from corn stover. One goal of our work is to set the stage for future air quality modeling in the preparation of advanced life cycle impact assessments (LCIA). For example, our approach uses existing chemical speciation factors[32] to describe pollutant emissions by chemical group. Another goal is to explore effects of model spatial resolution on the apparent distribution between urban and rural emissions.

MATERIALS AND METHODS

The approach presented here builds on the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model, version 1.8d1, from Argonne National Laboratory.[33] GREET models the energy use and air emissions of pollutants from activities that occur during fuel production and use. GREET, as configured for this analysis, is an attributional life cycle model, meaning that it includes

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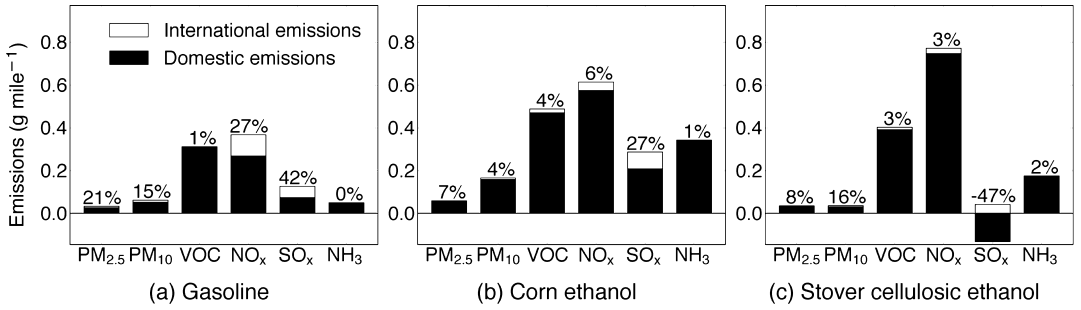

Figure 1. Amounts of emissions inside (domestic) and outside (international) the spatial modeling domain in units of grams emitted per vehicle mile traveled. Numeric labels indicate percent of life cycle emissions that are international. Our results are for domestic emissions only.

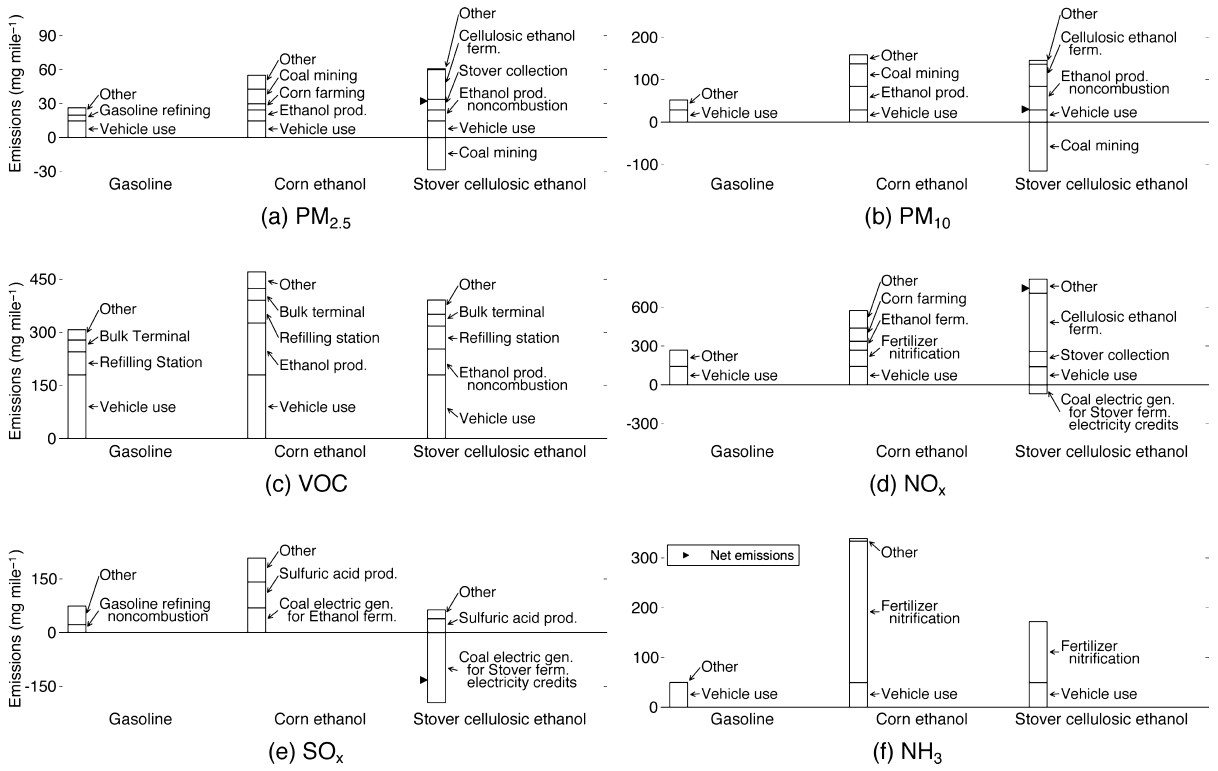

Figure 2. Fuel life cycle emissions, disaggregated by process. Plots exclude international emissions. For visual clarity, processes with emissions too small to display individually are lumped into an "Other" category; details regarding "Other" emissions can be found in SI S1. When a coproduct of a fuel production process displaces a competing product, the emissions from the life cycle of the displaced product are treated as negative emissions. For life cycles with negative emissions (e.g., stover cellulosic ethanol in plot (a)), net emissions are indicated by a small triangle on the left side of that bar. Abbreviations: trans. = transportation, ferm. = fermentation, gen. = generation, prod. = production.

emissions in fuel supply chains, but not those caused indirectly by market-mediated effects. Additional information about GREET is available elsewhere.[33]

GREET models five groups of air pollutant emissions: oxides of nitrogen (NO_x), nonmethane volatile organic compounds (VOCs), primary particulate matter less than 2.5 and 10 micrometers in diameter ($PM_{2.5}$ and PM_{10}, respectively), and sulfur oxides (SO_x). Following prior work,[29,40] we also include a sixth pollutant, ammonia (NH_3). $PM_{2.5}$ and PM_{10} inhalation can cause human mortality[34,35] and can decrease visibility. Particulate matter can be directly emitted ("primary $PM_{2.5}$") or can form in the atmosphere ("secondary $PM_{2.5}$"). VOCs can cause respiratory symptoms,[36] and NO_x can increase mortality risk.[37] VOCs and NO_x are precursors for ground-level ozone, which has also been linked to human mortality.[38,39] VOCs, ammonia, SO_x, and NO_x can each contribute to secondary $PM_{2.5}$. SO_x and NO_x can cause acid rain.

The number of fuels and fuel-processes one could study is large; here, we focus on a small number of fuels that are societally relevant, widely studied in previous research, and representative of a range of fuel types. Specifically, we present emission estimates for the production and use of gasoline, ethanol from corn grain through dry milling ("corn ethanol"), and ethanol from corn stover through cellulosic fermentation ("stover cellulosic ethanol"). Stover cellulosic ethanol is not currently produced on a large scale; we assume processes for the farming and refining of stover cellulosic ethanol to be colocated with the corresponding processes for corn grain ethanol. We present results using a functional unit of a vehicle-mile traveled.

We focus on adding to an existing life cycle inventory rather than refining its existing data. Accordingly, we use default GREET settings with the following exceptions: we assume that (1) corn ethanol plants use 100% natural gas process heat; (2)

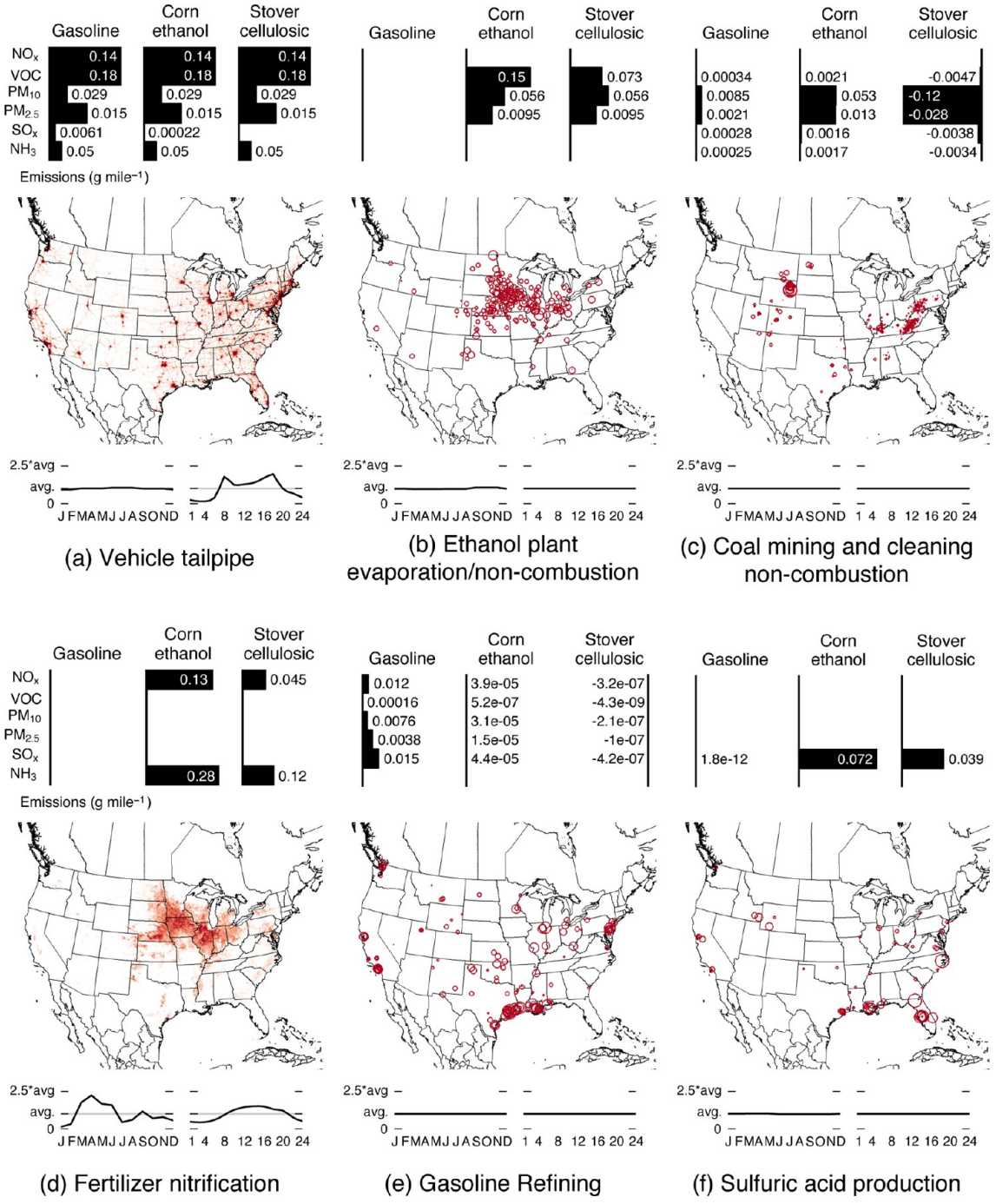

Figure 3. An overview of the spatial and temporal disaggregation for six of the highest emitting processes in the life cycles of the fuels discussed here. (Over 400 processes are described for each life cycle; see SI S1 and S3 for processes not shown here.) The bar charts show emissions by pollutant in grams per vehicle mile traveled; each pollutant has its own bar length scale, and scales are consistent among panels. The maps show the points or areas where the process occurs, with either the grid cell color intensity or the area of the circle proportional to the fraction of total activity occurring at each location. Line plots indicate the relative amount of emissions by month of the year and hour of the weekday. For fertilizer nitrification, temporal profiles vary by location; the average values are plotted for each month. "Stover cellulosic" = stover cellulosic ethanol.

the ethanol produced is 100% ethanol without denaturant; however, because tailpipe emissions depend on blend level, we use tailpipe emission factors for E10 (i.e., a mixture of 90% gasoline, 10% ethanol) for the ethanol fuels (results for E85 [85% ethanol, 15% gasoline] can be found in the Supporting Information (SI) S1); (3) gasoline production is 100% conventional (i.e., not reformulated) gasoline; and (4) crude oil production is 100% conventional crude (most oil sands production occurs outside of our spatial modeling domain and is therefore excluded from our spatial analyses). Vehicle energy-efficiency and emissions are the same for all fuels, except SO_x emissions, which are lower for ethanol vehicles. Efficiencies and emissions factors reported here are for year 2010.

Transportation fuels used in the U.S. are delivered by a global supply chain, and their associated pollution likewise occurs worldwide. GREET includes hundreds of unit processes involved in fuel production and use, and reports life cycle emissions as global totals. Here, we focus on the fraction of life

cycle emissions that occurs in the continental U.S. and its neighboring waters. To estimate GREET emissions inside that boundary, we multiply individual GREET unit process emissions by the ratio of domestic production of their products (refs 41−43, excluding Alaska and Hawaii) to total consumption. We use the same factor to adjust upstream emissions for each process. For ocean tanker emissions, we consider emissions within the continental United States' Exclusive Economic Zone (within 200 nautical miles from shore) to be within the spatial modeling domain. We assume that ocean tankers acquire 50% of their fuel outside of the spatial modeling domain. Figure 1 shows emissions allocated within and outside of the spatial modeling domain. Most emissions are domestic. The median value in Figure 1 is 94% domestic and 6% international. SI S2 provides similar details for all processes; as in Figure 1, in all cases, most emissions are domestic. Figure 2 shows domestic emissions for select processes; further details are in SI S1.

Spatial Disaggregation. In this attributional approach, emissions are assumed to come from existing infrastructure. The fraction of emissions allocated to each facility is assumed to be equal to the fraction of total U.S. production at that facility. For example, a refinery that currently produces 5% of the gasoline in the U.S. would have 5% of gasoline production emissions allocated to it. We obtain information on the locations and average U.S. production of coal mines,[44] crude oil and natural gas extraction,[45] natural gas processing,[46] petroleum and natural gas pipelines,[2] fertilizer production,[47] sulfuric acid production,[48] pesticide production,[2] biorefineries,[49] petroleum refineries,[50] corn and soy farm locations,[51] and vehicle use,[52,53] and use it to spatially distribute the emissions by life cycle stage to a user-defined grid or within geographical polygons (e.g., states, counties, regions, etc.).[54] A 2010 calendar year industry is modeled using available data from between 2002 and 2011 (see SI S2 for more detail). To accomplish this spatial (and later temporal) assignment of emissions, GREET data and equations are rewritten as a program in the Python language to allow process-specific emissions tracking for at least 97% of emissions for each fuel. We present results for a 12-km grid resolution, with comparisons to 4- and 36-km resolutions in SI S2. References for the spatial data used for each process, and the year each data set was collected, are in SI S2. For processes that use electricity, we allocate the electrical generation emissions to generators from the U.S. EPA's eGRID database[55] located in the same North American Reliability Corporation (NERC) region as the end-use process. We allocate emissions from transportation via truck, rail, and barge using a combination of geographic network analysis[54] and linear optimization[56] techniques. The method used is described in more detail in SI S2. Pipeline and ocean tanker emissions are allocated to existing emission locations.[2] Coproducts, such as distiller's grain with solubles (DGS) production for corn ethanol and excess electricity production for stover cellulosic ethanol, are treated in GREET using a system expansion approach and are assumed to displace emissions from competing products (i.e., soy production or electricity generation). We allocate negative emissions resulting from displacement using the same methodology as for positive emissions. Each emission source is additionally classified as ground-level or elevated; elevated pollutant releases are assigned average values for U.S. electricity generating units: height, 23 m; diameter, 3 m; temperature , 456 K; exit velocity, 1.8 m s^{-1}.[2] Refer to SI S1 for the height classification of each process. Process-specific spatial and temporal information is summarized in Figure 3 for six of the more than 400 processes; additional details are in SI S3.

Temporal Disaggregation. The time at which air pollutant emissions occur can be an important determinant of their ultimate impacts. For instance, conversion rates of VOCs and NO_x into ground-level ozone are greater during hot summer days than at other times. In contrast, emissions of $PM_{2.5}$ and its precursors may result in higher concentrations during winter than during other times because dilution rates tend to be lower in winter.[57,58] We link each of the processes shown in SI S1 with process-specific temporal profiles[2,59] to allocate emissions by month, day-of-week, and hour-of-day, with different allocations for weekdays and weekends. Figure 3 shows temporal profiles for several processes.

Chemical Disaggregation. The species categories that GREET outputs (VOCs, NO_x, SO_x, $PM_{2.5}$, and PM_{10}) are aggregates of many individual chemicals or pollutant types. Such broad categories can limit the accuracy of an impact analysis. For instance, the combustion of gasoline and ethanol both produce VOCs, but they produce different types of VOCs, with varying toxicity, reactivity, and ozone-production potential. The combustion of gasoline and ethanol both produce $PM_{2.5}$ and its precursors, but certain types of $PM_{2.5}$ cause atmospheric cooling (e.g., sulfate aerosols) while others cause atmospheric warming (e.g., black carbon aerosols).[60] To develop the inventory presented here, we link each of the processes shown in SI S1 with chemical speciation profiles[32] to disaggregate the emissions into 34 chemical species groups according to the Carbon Bond 2005 (CB05[61]) chemical mechanism. CB05 speciates emissions into the following groups:

- **VOCs**: acetaldehyde, higher aldehydes, benzene, methane, ethene, ethane, ethanol, formaldehyde, internal olefins, isoprene, methanol, olefins, paraffins, sesquiterpenes, terpenes, toluene, xylene, nonreactive VOCs, nonvolatile VOCs, and unknown/other VOCs
- **$PM_{2.5}$**: black carbon, nitrate particulates, organic particulates, sulfate particulates, and unclassified $PM_{2.5}$
- **NO_x**: NO and NO_2
- **SO_x**: SO_2 and $SO_{4,g}$.

PM_{10} and NH_3 are included without speciation.

RESULTS

Figure 1 shows fractions of emissions occurring outside of the spatial modeling domain for each fuel. (These and all other results show emissions of air pollutants, which may or may not be directly correlated with changes in ambient pollution levels.) As mentioned above, emissions that occur outside of the spatial modeling domain (contiguous U.S. and surrounding waters), are excluded from results below. Excluding international emissions has the largest effect on the gasoline life cycle. This result is because we model 96% of emissions from transportation of crude oil by ocean tanker as occurring outside the spatial modeling domain. International tanker emissions account for 34% of SO_x, 16% of NO_x, 14% of $PM_{2.5}$, and 8% of PM_{10} gasoline life cycle emissions. However, these ocean tanker emissions occur over the open ocean where human exposure is very low,[26] so the exclusion of these emissions will likely not noticeably affect estimates of total human exposure. Other notable spatial modeling domain exclusions include 28% of sulfuric acid production for fertilizer,[62] accounting for 12% of

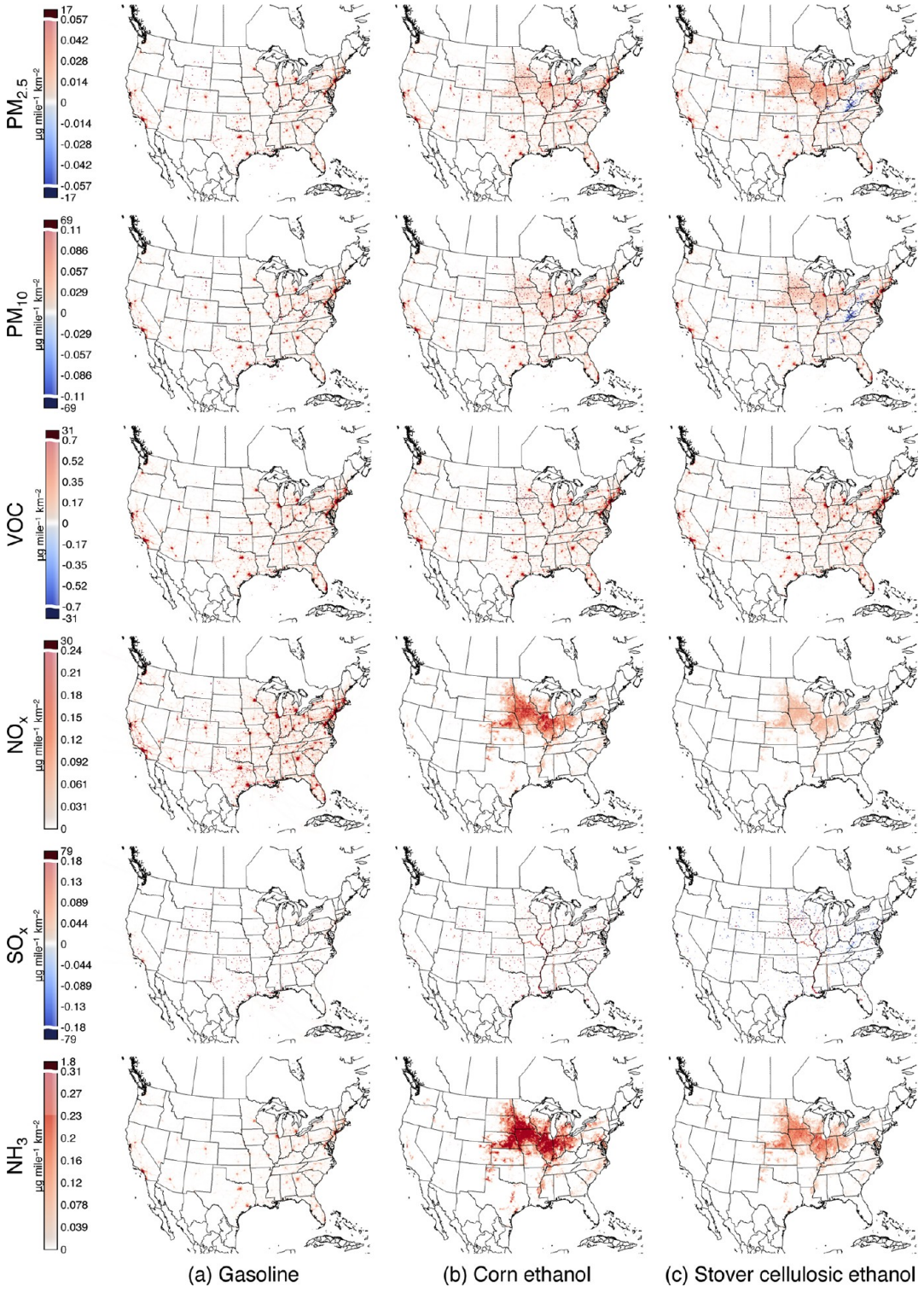

Figure 4. Annual total life cycle emissions for three fuels. For ease of viewing, each linear color scale contains a discontinuity at the 99th percentile of emissions.

corn ethanol and 20% of stover cellulosic ethanol SO_x life cycle emissions, and 56% of crude oil extraction,[63] accounting for 6% of NO_x emissions from the gasoline life cycle. All other processes either occur completely within the modeling domain or comprise a negligible fraction of the life cycle total emissions.

Figure 4 shows 12 km resolution gridded emissions for the gasoline, corn ethanol, and stover cellulosic ethanol fuels. In general, gasoline emissions tend to be correlated with vehicle use and so are distributed in or near urban centers. Ethanol emissions tend also to be correlated with ethanol production and so are concentrated in the Midwest "Corn Belt". The area along the Kentucky/Virginia border extending into West Virginia experiences a reduction in $PM_{2.5}$ emissions (shown in blue in Figure 4) owing to reduced coal mining activity caused by excess electricity generation in biorefineries. Excess

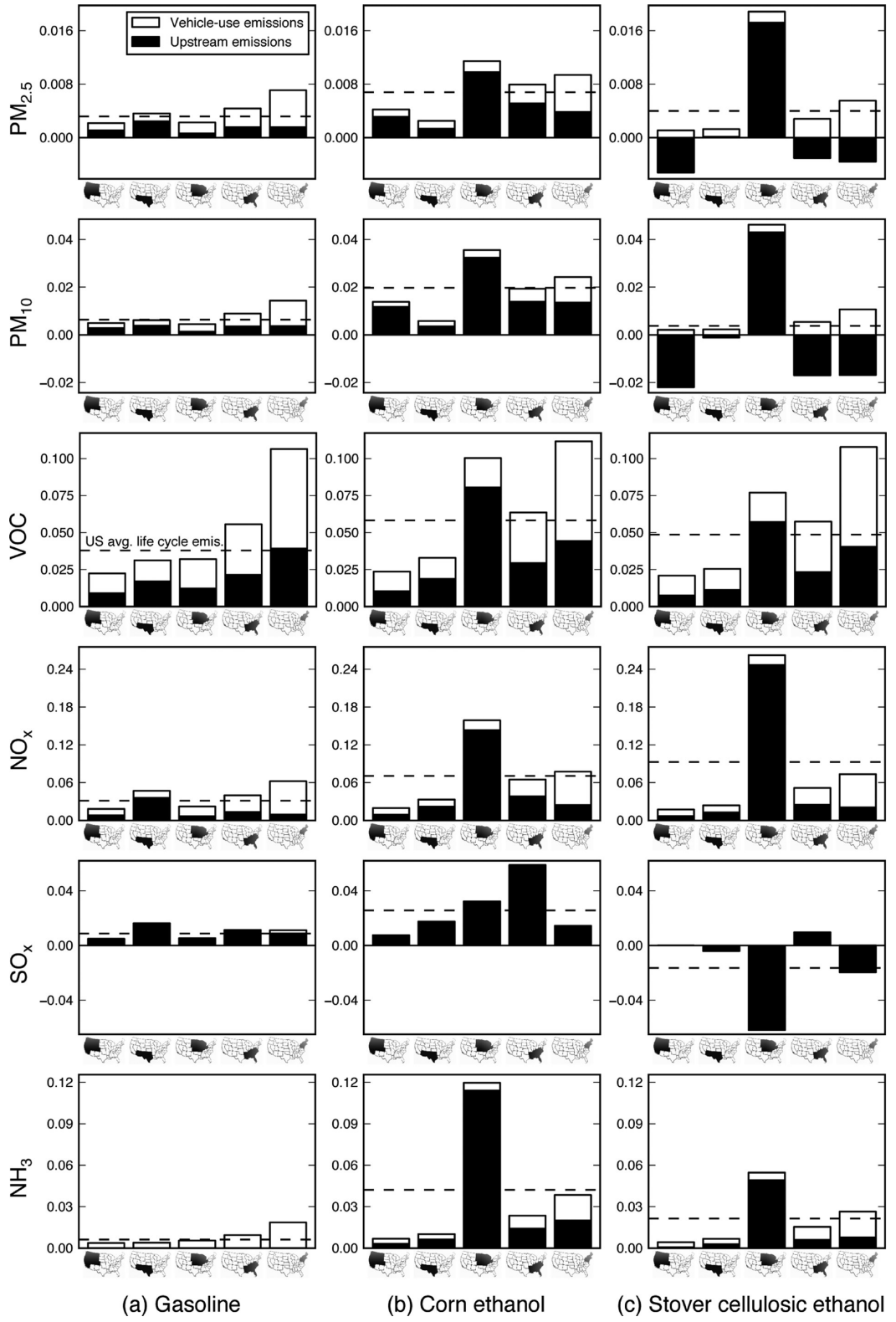

Figure 5. Contributions of U.S. regions to total life cycle emissions for three fuels (micrograms emitted per vehicle-mile traveled per square kilometer land area). Dashed lines show U.S. average emissions. Refer to SI S2 for a version of this figure with units of g mi^{-1}. Key: Northeast, Midwest, Southeast, Southwest, West.

electricity is sold to the electrical grid and assumed to offset electricity produced elsewhere.

Figure 5 shows emissions contributions by region of the U.S. For all three fuels, the greatest intensity of emissions per land area occurs in the Northeast for VOCs, owing to the large portion of total vehicle miles traveled per land area occurring there. See SI S2 for the fraction of vehicle miles traveled in each region. The Midwest receives a large amount of emissions for both ethanol fuels, owing to ethanol fermentation plants and ammonia emissions from fertilizer nitrification. For the

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Midwest, emissions are lower for gasoline than for ethanol, with the exception that SO_x emissions are negative (i.e., reduced) for stover cellulosic ethanol owing to excess electricity generation at fermentation plants. SO_x emissions in the Southeast for corn ethanol are mainly attributable to Florida-based sulfuric acid production for phosphate fertilizer. The Southwest and West regions generally do not receive large proportions of pollutant emissions for any of the three fuels (exception: SO_x emissions for gasoline).

Emissions are spatially disaggregated by allocating them to cells in a raster grid. As has been previously noted,[15] we observe that the resolution of the grid used can influence the apparent locations of emission. SI Figures S2-1 and S2-2 show the dependence of emissions allocated to urban areas on the spatial scale of the grid used for allocation and compares the results to the urban emissions given by GREET.[28] Overall, increasing grid resolution leads to an increased allocation of emissions to urban areas, suggesting that a coarse grid tends to artificially dilute urban emissions to the surrounding rural areas. See S2 for further discussion.

Figure 6 shows temporal profiles for fuels and pollutants discussed here. Pollutant emissions from the gasoline life cycle do not vary appreciably by month. For the corn ethanol life cycle, however, there is a spike in NH_3 and NO_x emissions in the spring, corresponding to fertilizer application. This pattern is also true to a lesser extent for stover cellulosic ethanol. All fuels show a slight decrease in emissions on weekends. Weekday emissions commonly show a bimodal distribution around the morning and evening rush hours owing to increased vehicle tailpipe emissions at those times. For fuels and pollutants where farming activities are a major contributor, however, the weekday and weekend emissions are unimodally distributed around the daylight farming hours.

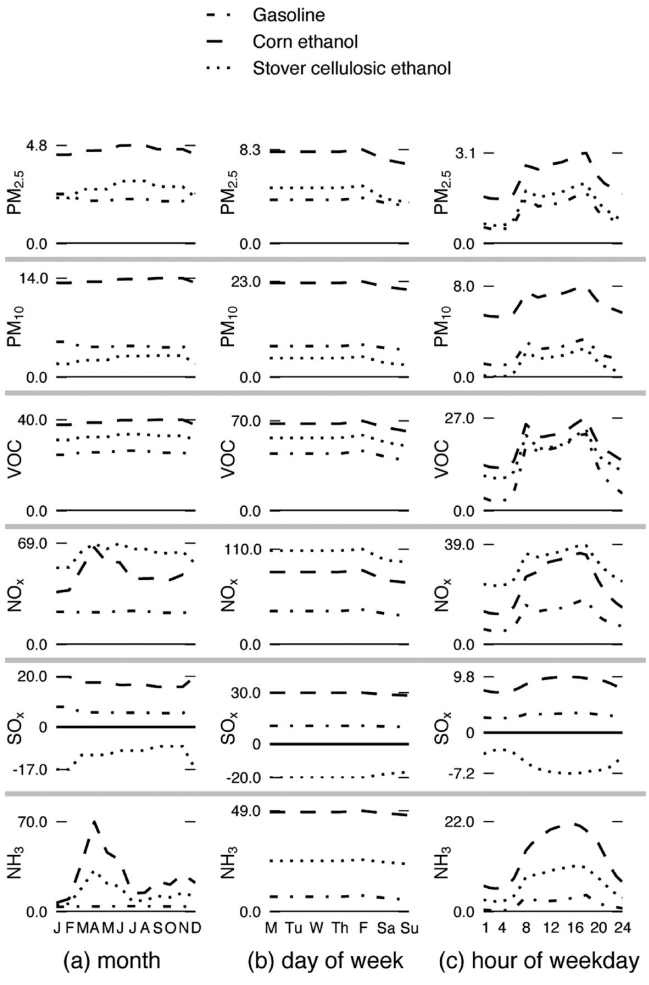

Figure 6. Temporal profiles of life cycle emissions (mg emitted per vehicle-mile traveled) by month of year, day of week, and hour of day (weekday). Results by hour of day (weekend) are in SI S2.

Our chemical speciation reveals the following. Although stover ethanol emits the lowest total amount of $PM_{2.5}$ of all three fuels, it emits more black carbon (15 mg mi^{-1}), a species of fine particulate matter that contributes to atmospheric warming, than either of the other two fuels (gasoline: 4.5 mg mi^{-1}, corn ethanol: 10). Stover cellulosic ethanol also emits the lowest amount of sulfate aerosols (−1.3 mg mi^{-1}; gasoline: 1.9, corn ethanol: 3.8), which cause atmospheric cooling. Emissions of ethanol are 30 000−40 000 times higher for the ethanol fuels than for gasoline; ethanol in the atmosphere may be oxidized to form acetaldehyde (a carcinogen). However, emissions of benzene (another carcinogen[64]) are higher for gasoline than for the ethanol fuels (the relative amounts by fuel depend on the ethanol feedstock and the blend level of the final fuel). Full results for chemical speciation, including for 85% ethanol blends (E85), are in SI S1.

DISCUSSION

We have presented a spatially and temporally explicit life cycle inventory for transportation fuels. Prior life cycle inventories were typically presented at global, national, or regional levels, which is sufficient for understanding global processes such as climate change and fossil fuel depletion, but is insufficient for the analysis of local processes such as air pollution. The spatially and temporally explicit LCI presented here not only provides the level of detail necessary to perform detailed LCIA of air pollutant emissions, it also gives information on spatial and temporal trends that can be useful in policy making and regulation. For instance, in the U.S., implementation plans for coming into compliance with air quality standards are generally determined by individual states. Spatially and temporally explicit LCA can help state-level policy makers identify potential sources of air pollutant emissions within their jurisdictions and create appropriate regulations. Such information is not delivered by conventional LCA approaches.

The framework presented here outputs gridded, time-resolved emissions files, which is an important step toward photochemical dispersion modeling. For example, U.S. production and consumption of stover cellulosic ethanol would increase emissions of NO_x, NH_3, and $PM_{2.5}$ in the Midwest, but would decrease SO_x emissions in the same region. All four of these species influence ambient concentrations of $PM_{2.5}$, it is unclear a priori whether the net change in $PM_{2.5}$ concentrations will be positive or negative in this region. Photochemical dispersion modeling can help answer this question.

Our choice of spatial modeling domain (continental U.S.) by definition restricts our study. However, we do not see this aspect as a major limitation because most emissions occur within our boundary, and because most of the excluded emissions occur over the open ocean, for which human exposures are much lower than for emissions on land.[26] This same domain has been used in prior regulatory analysis.[65] At present, lack of computational power and accurate input data

make it impractical to extend the system boundaries to the entire world. For future work, a nested approach (detailed spatial treatment of emissions within the modeling domain; coarser resolution outside of the domain) could prove useful. A further limitation of this study is that owing to limited data availability, the spatial data used here represent a range of years (2002−2011; see SI S2 for details). Finally, uncertainty and variability in the spatial, temporal, and chemical speciation data used here contribute to the overall uncertainty in the life cycle inventory, but this information is generally unknown or unreported.

Our work considers supply chain emissions of existing production. GREET, and by extension the framework presented here, performs an exclusively attributional (static) LCA for non-GHG air pollutants. We do not include indirect (market-mediated) effects. An example of an indirect effect would be if corn ethanol production in the U.S. increases global grain prices, causing emissions from the burning of tropical rainforest to grow crops. A consequential (dynamic) LCA, which we do not do, would aim to capture indirect effects. We assume here that all processes occur at existing production locations; in reality, new production may cause new facilities to open, or existing facilities to close or change locations. We assume that cellulosic biorefineries for stover cellulosic ethanol are colocated with existing corn ethanol biorefineries; in reality, the difficulty of transporting corn stover may cause biorefineries to be smaller and closer to cornfields.

We have focused here on the air pollutant implications of the choice between ethanol and gasoline as a transportation fuel. In general, methods presented here can provide insight into any spatially or temporally inhomogeneous environmental impact categories, such as water quality and availability, soil properties, or wildlife habitats. They can also be expanded to study specific processes that affect those impact categories, such as agriculture and food production, building construction, or electricity generation; the possible applications are only limited by the availability of data.

■ ASSOCIATED CONTENT

Supporting Information

Process-specific, chemically speciated, and state and urban area specific emissions data (S1a−c, Excel format), supplemental text and figures, and process-specific maps (S2 and S3a−c, pdf format) for gasoline, corn ethanol, and stover cellulosic ethanol. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hill0408@umn.edu.

Notes

The authors declare no competing financial interest.

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