

Assessing County-Level Water Footprints of Different Cellulosic-Biofuel Feedstock Pathways

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Supporting Information

ABSTRACT: While agricultural residue is considered as a near-term feedstock option for cellulosic biofuels, its sustainability must be evaluated by taking water into account. This study aims to analyze the county-level water footprint for four biofuel pathways in the United States, including bioethanol generated from corn grain, stover, wheat straw, and biodiesel from soybean. The county-level blue water footprint of ethanol from corn grain, stover, and wheat straw shows extremely wide variances with a national average of 31, 132, and 139 L of water per liter biofuel (L_w/L_{bf}), and standard deviation of 133, 323, and 297 L_w/L_{bf} , respectively. Soybean biodiesel production results in a blue water footprint of 313 L_w/L_{bf} on the national average with standard deviation of 894 L_w/L_{bf} . All biofuels

show a greater green water footprint than the blue one. This work elucidates how diverse spatial resolutions affect biofuel water footprints, which can provide detailed insights into biofuels' implications on local water sustainability.



1. INTRODUCTION

With the goal of reducing greenhouse gas emissions and foreign oil dependence, the Energy Independence and Security Act (EISA) has set the target of blending 36 billion gallons (or 136 billion L) of renewable fuel into the U.S. transportation fuel mix, in which 44% should be contributed by the cellulosic ethanol and at least 3% from biodiesel.¹ Although the large-scale production of biofuels and their economically feasible commercialization currently face significant technical challenges,² studies still positively anticipate that cellulosic biofuel alone will replace 10% of the national petroleum demand by 2022, with the ultimate potential to replace 30% of current national fuel demand by 2030.^{3,4} As for biodiesel, a production gap of 2.6 billion L remains from 2010 to 2022.⁵ The production schemes for bioethanol and biodiesel have put the U.S. on the global map as the number one second-generation bioethanol producer and the second largest biodiesel producer in the world, according to OECD-FAO's projection to 2020.⁶ However, the water demand associated with the increase in biofuel production is one of the major environmental concerns, and withdrawal of water for global biofuel production is projected to increase by 74% in 2017 as compared to 2009 if agricultural and irrigation schemes remain the same.⁷

In a recent study by Wu et al.,⁸ the authors summarized nine significant papers on the water footprint of biofuels in the U.S. The results indicate that all of the studies use spatial resolution at the state level or above, and the studies with national coverage include only three types of feedstock at most. Among the most studied feedstocks, the water footprint for corn is analyzed in all nine studies,⁹⁻¹⁷ followed by switchgrass^{13,17}

and corn stover.^{9,15} The limited selection of feedstocks makes it difficult for these studies to comprehensively support decision-makers in determining sustainable pathways to achieving renewable-energy goals. Also, the spatial resolution in these studies is not sufficient to reflect local water impact associated with biofuel production.

In addition, the lack of a consistent water-footprint calculation framework makes comparison among different study results challenging. For instance, to quantify water embodied in the biofuel, some studies refer to the total withdrawals,^{10,15,16} whereas others aim to estimate consumptive water.^{9,11-14,17} In terms of water characterization, gray-water estimation still remains as a major challenge and has gained little attention. A comprehensive study conducted by van Lienden et al.¹⁸ estimated blue and green water footprints for first-generation bioethanol and biodiesel production on a global scale. However, the authors state that gray water was excluded from their study because of the lack of data. A recent work by Mekonnen and Hoekstra¹⁹ compiled a large water footprint database for multiple agricultural products using a grid-based irrigation modeling approach. The study relies on stochastic-model generated precipitation and temperature to simulate crop yield and water use. For gray water estimation, Mekonnene et al. assume a national average fertilizer application rate for each grid across the entire country, and

10% of the nitrogen fertilizer applied to the fields is leached into water bodies with a background nitrogen concentration of zero ppm regardless of the crop types. However, a previous study states that background nitrogen concentration in the streams and fertilizer application rates vary significantly from region to region in the U.S., by which the nutrient loadings on water bodies can be diverged.²⁰

Therefore, to better assist national energy and environmental decision-makers in selecting suitable biofuel feedstock by taking local water characteristics and agricultural practices into account, our study aims to estimate the national biofuel water footprint on the county level, and to examine the extent of spatial resolution and its impact on water footprints with the most available agricultural and irrigation data in the U.S. The key production systems assessed by this study include a future multiple-production system utilizing both grain (corn grain) and agricultural residue (corn stover and wheat straw) as feedstock, and a single-production system deriving soybean for fuel without using its residue. Thus, a total of two types of cellulosic-based and two types of conventional feedstock are examined. Biofuel water footprints are then presented on a liter of water per liter of biofuel (L_w/L_{bf}) basis.

2. METHODS

The blue-water volume in the system accounts for consumptive irrigation water lost through conveyance, operation, crop evapotranspiration (ET), and process water losses. Green water, however, refers only to the rainfall amount lost through crop ET in our cases. Unlike blue and green water volumes, which estimate actual water volume lost from the system, gray water is the virtual water volume indicating the level of pollution, agricultural pollutants in particular, associated with a product or service.²¹

2.1. Green and Blue Water. The detailed calculation of blue and green water volumes follows the procedure proposed in the study of Wu et al.⁸ To distinguish between green and blue water in the crop-growing stage, the total crop water demand associated with ET is estimated using the Penman—Monteith model. Proportional ET satisfied by effective rain is classified as green water, and the rest hence requires blue water from irrigation input to support crop growth. For each target feedstock, the consumptive irrigation computed using this approach plus the irrigation conveyance, operation losses, and returned flow published by the USGS²² equals the estimated irrigation withdrawals, which are further calibrated using state-level irrigation data reported by the USDA in 1998, 2003, and 2008^{23–5} (see Supporting Information Section 1).

In a biorefinery, the amounts of blue-water process water used to produce one liter of biofuel from corn, stover, and soybean are 2.72 L,²⁶ 5.40 L,²⁷ and 0.77 L,²⁸ respectively. Wheat-straw bioethanol production via biochemical conversion is similar to the stover conversion process.

2.2. Gray Water. The gray-water volume accounts for the virtual quantity required to assimilate the pollutant load from the permissible standards down to the natural background concentration.²¹ In this study, we use nitrogen as an indicator for the estimate of gray water, which is a common approach found in previous studies.^{19,29} In addition, corn and wheat fields receive more nitrogen fertilizer per hectare than phosphorus in the U.S. by over two folds.³⁰ The fraction of nitrogen fertilizer loss to water body resulted from the leaching process is also significantly higher than that of phosphorus.³¹ Therefore, nitrogen is a representative indicator in quantifying the water-

quality aspect associated with biofuel production. We establish the county-level nitrate loading in water body resulting from feedstock fertilizer application and the level of natural background nitrate concentration in the streams based on available data (see SI Section 2).

For corn and soybeans, we take two approaches to determine the nitrate loadings associated with each type of feedstock, depending on the location of the county. If a county is situated within the Upper Mississippi River Basin, then a fraction of nitrate leached into streams (output) in total nitrate fertilizer applied in the fields (input) (NOI) is determined based on a SWAT model simulation.³² Otherwise, we adopt the NOI from a series of SPARROW-based models established by the USGS using 1992 and 2002 information^{33–38} (see SI Table S1). In addition, corn-stover not only receives fertilizer during its growth but also the supplemental fertilizer to make up the nutrient loss due to stover removal. The gray water of stover accounts for the effect from both applications.

2.3. Feedstock Water Allocation. The water consumed by crops for growth is attributed to the entire plant including grain and stover, and is linearly related to the mass production in each part of a crop plant. It is conceivable that blue, green, and gray water resulted from the growth of the entire crop plant should be allocated to grain and residue, if both parts are utilized as biofuel feedstocks. In this case, each material is proportionally responsible for the environmental burden associated with the production process.

Given this principle, the mass-based allocation method is suitable for feedstock water allocation between grain and residue for corn and wheat, which can be achieved by using a crop's harvest index (HI) (wt/wt%), defined as the ratio of grain mass to the mass of the total aboveground plant^{27–30} (see SI Section 3). The green, blue, and gray water volumes associated with each feedstock in the growing stage can be further allocated between grain and the collected residue based on a crop's HI. As for soybeans, because its residue is not considered as a feedstock, the water footprint associated with its growth is entirely allocated to the beans.

2.4. Coproduct Partitioning. An accurate account of the water consumed by biofuel coproducts is essential to achieve reliable water footprint results for biofuels. Five distinctive coproduct partitioning methods are reviewed, including system expansion, process energy, mass, product energy content, and product market value. Given the nature of biofuel produced from agricultural crops, we select system expansion in conducting the coproduct allocation (see SI Section 4).

In our analysis, we assume the production of distillers grains with solubles (DDGS) in the corn-ethanol dry milling can displace corn, soybean and urea in the animal feeds.² The glycerin produced in the soybean biodiesel processing can displace epichlorohydrin glycerin, which can be credited back to soybean biodiesel blue water footprint. For the cellulosic feedstocks of corn stover and wheat straw, bioelectricity is generated as a coproduct during the biochemical conversion process (see SI Section 4).

2.5. Water Resources. With respect to the water cycle, blue water is the critical variable that is highly governed by anthropogenic decisions and activities. We specifically classify the percentages of blue water sourced from groundwater and from surface water, on the basis of county-level water use data for 2005 published by the USGS.³⁹ The ratios between groundwater and surface water in the irrigation and industrial sectors are compiled for estimation of blue-water sources in the

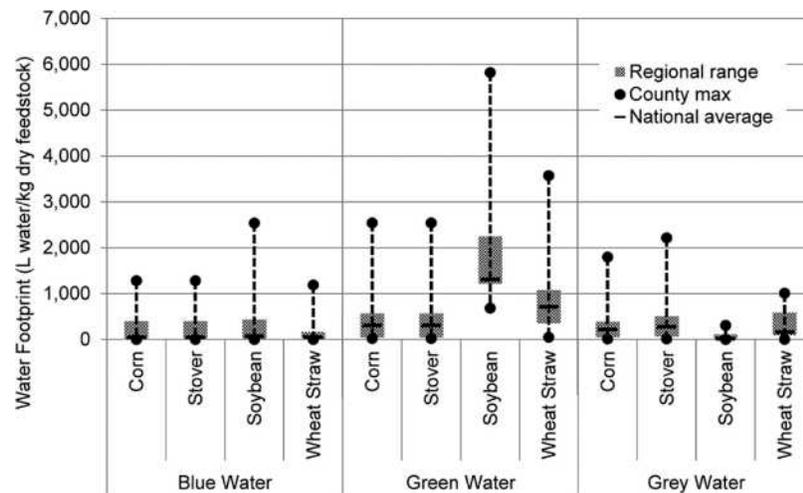


Figure 1. Blue, green, and gray water, in liters per kg dry feedstock, during the crop-growing stage. The horizontal bars represent the national average values. The dashed lines show the variances of feedstock water footprints on a county basis. The shaded bars represent the regional range of variances. The position of the national-average water footprint of each feedstock indicates the weight-shift effects caused by the dominating feedstock-producing counties.

crop-growing and refinery stages, respectively. If the industrial water-source data are not available for a given county, then the source ratio representing the public sector is applied instead.

2.6. Data Sources. The climate data required for green and blue water estimation are primarily derived from the National Climate Data Center⁴⁰ for the period of 1970 to 2000. Crop data and irrigation information are available from the National Agricultural Statistics Service,⁴¹ Census of Agriculture,⁴²⁻⁴⁴ and Farm and Ranch Irrigation reports.²³⁻²⁵ We use the average of 1998, 2003, and 2008 data as a baseline. To further distinguish water sources extracted by irrigation and refinery operations, the USGS report on water use in 2005 is adopted.³⁹

Gray-water estimation requires fertilizer application information for each feedstock type, which is available from the database hosted by the Economic Research Service of USDA.³⁰ We use 2005 fertilizer application data to develop the baseline for corn stover, and 2006 data for soybeans and wheat, reflecting data availability. To estimate the ratios of nitrogen loading in fertilizer input (NOI) for each type of feedstock on the county level, values can be derived from studies previously conducted by Argonne National Laboratory³² and USGS.³³⁻³⁸

3. RESULTS

This water footprint study includes gray water in addition to blue and green water for all the lower 48 states, with four feedstock pathways, at county-level resolution. This study assesses cellulosic biofuels based on and calibrated by local agricultural and environmental data, to which the previous global scale studies^{11,19} fall short to address due to data availability. Thus, our study is based on the water footprint methodology proposed by Hoekstra et al.²¹ but with extensive local data to reflect local agricultural practices with increased spatial resolution and to address model validation. For example, the theoretical blue water for irrigation estimated by the evapotranspiration model has been verified by using the field survey data, which allows us to improve the theoretical blue water and reflects water loss through agricultural practices including conveyer losses, irrigation losses, and water conservation. We also quantify gray water associated with biofuel production with the improved data set. The previous gray water estimation relies on the assumptions including (1)

crops receive the same amount of nitrogen fertilizer per area in a country, (2) a uniform leaching fraction is applied across a country, and (3) background nitrogen concentration equals to zero.^{19,29} In this work, we are able to collect and process additional data needed to fill the data gap so that the assumptions are no longer needed.

Another difference between current and previous studies is the system boundary. This study is to quantify biofuel water footprint from a future multiple production system that utilizes both grain and agricultural residue as feedstock, which provides straightforward comparison in the biofuels' water implications using different feedstocks. We also factor blue and green water into water resource aspects and provide a picture to illustrate how biofuel may shape future water sustainability. Notably, all of the county-level variances in water footprint presented in the following sections are directly accounted without strategically sourcing feedstock from preferred locations to reduce water impact.

3.1. Water Footprint in the Crop-Growing Stage.

During the crop-growing phases, green water shows the greatest variances, followed by gray water and then blue water, in terms of volume per kg dry feedstock disregard the next unit process (Figure 1). For blue water, soybean and corn grain or stover appear to have the highest county-level variances, ranging from 0.01 to 2539 L/kg and 0.01 to 1283 L/kg, respectively. Corn grain and stover also show the greatest gray-water variance, ranging from 9 to 1799 L/kg for corn grain and 11 to 2215 L/kg for stover. The difference in gray-water distributions between corn grain and corn stover is greater than that in green or blue water because stover is responsible not only for the gray water associated with fertilizer used during the corn-growing stage, but also for that applied as a nutrient supplement to soil after the stover is removed.

In terms of green water, corn grain and stover appear to have the least county variances ranging from 21 L/kg to 2543 L/kg, followed by wheat straw and soybean of 50-3572 and 682-5821 L/kg, respectively. The distribution of water footprints in feedstock growing stages leads to a larger variances of the soybean biodiesel in the blue and green water category than other biofuels using corn, corn stover, and wheat straw. However, soybean biodiesel appears to have the least gray water

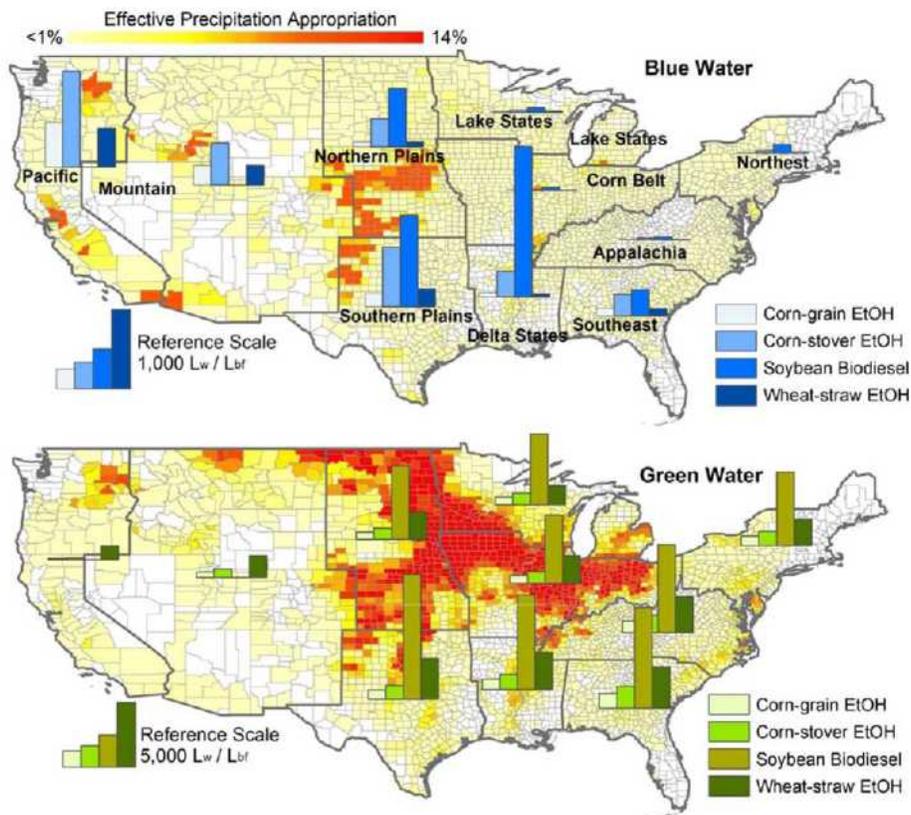


Figure 2. Liters of blue and green water per liter of biofuel by feedstock in various regions. The blue and green water footprints are aggregated to the regional scale by feedstock. The background color gradient indicates the fraction of blue- and green-water appropriating a county's effective precipitation, assuming 30%, 24%, 12%, and 30% of corn grain, corn stover, soybeans, and wheat straw, respectively, are consumed by the biofuel production. The white background color indicates the lack of crop data, hence, equivalent to zero blue and green water. Notably, the results apply to the production systems that corn grain and stover are both harvested for biofuel, wheat residue is used for biofuel and grain for food (not presented in this study), and soybean for fuel (residue not harvested).

variances due to the low fertilizer demands during soybean growing stages. The wide distribution of feedstock water-footprint variances indicates the importance of elucidating biofuel water demand by taking spatial resolution into account.

3.2. Comparison of Biofuel Blue and Green Water Footprints by Pathways. Ethanol produced from corn grain, stover, and wheat straw applying a multiple-production system, where both grain and residue are harvested for biofuel, has the national average blue water footprint of 31, 132, and 139 L of water per liter ethanol (L_w/L_{EtOH}), respectively. Soybean biodiesel, which is described as a single-production system using grain for fuel without harvesting residue, appears to have an average blue water footprint of 313 L of water per liter biodiesel (L_w/L_{dst}). Overall, blue and green water are found to be geographically complementary across all biofuel feedstocks (Figure 2).

At the county level, ethanol from corn grain and stover shows blue water footprint ranging from -587 to 1809 L_w/L_{EtOH} and 5 to 3896 L_w/L_{EtOH} , respectively. As the major corn producer in the U.S., the Corn Belt region results to corn-grain and stover ethanol blue water ranging from -9 to 122 L_w/L_{EtOH} and 5 to 424 L_w/L_{EtOH} , respectively, comparing that with the highest blue water of 1809 and 3896 L_w/L_{EtOH} for corn-grain and stover ethanol at a county located at the Southern Plains. Note that some counties may show negative blue water owing to the received water credits higher than water that is consumed. The county-level blue water of soybean biodiesel and wheat-straw ethanol ranges from 0.1 to 11 107 L_w/L_{dst} and

5 to 3615 L_w/L_{EtOH} , respectively, in which the highest values occur at two counties located at the Northern Plains and the Mountain regions. In contrast, Appalachia region can produce soybean biodiesel and wheat-straw ethanol with the lowest blue water footprint ranging from 0.1 to 380 L_w/L_{dst} and 5 to 101 L_w/L_{EtOH} , although it is not a dominating soybean or wheat producer (Figure 2). The highest blue water of soybean diesel and wheat-straw ethanol appears to be 11 107 L_w/L_{dst} and 3615 L_w/L_{EtOH} .

At the regional average, soybean biodiesel results in blue water from 37 L_w/L_{dst} at the Appalachia region to 1898 L_w/L_{dst} at the Delta. Ethanol produced from corn grain, corn stover, and wheat straw that grown in the Pacific region have the largest blue-water footprints of 563, 1211, and 491 L_w/L_{EtOH} , respectively, comparing that with the lowest of 6 and 16 of corn-grain and corn-stover ethanol at the Corn Belt and 6 L_w/L_{EtOH} of wheat-straw ethanol at the Appalachia. This result echoes the analyses found by Chiu et al.¹⁰ for corn ethanol, although the calculation approach and spatial resolutions are different. As a complementary result, green-water footprint for the ethanol produced at Pacific appear to be the lowest, ranging between 87 L_w/L_{EtOH} using corn grain and 130 L_w/L_{EtOH} from corn stover.

3.3. Gray-Water Spatial Variation. The geographical distribution of gray-water volume and its numerical range is a result of not only fertilizer input, but also fertilizer leaching patterns and the characteristics of local natural background nitrate concentrations. Therefore, the Appalachia, Delta, and

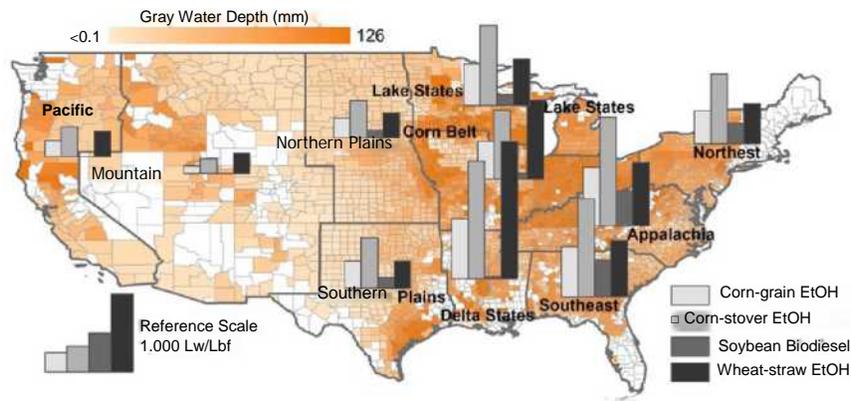


Figure 3. Total biofuel gray-water footprints and attributions for different feedstocks. The background color indicates the harvest-area weighted total gray-water depth associated with all the studied fuel feedstocks, following the same crop consumption assumption as in Figure 2. The length of the bars represents liters of gray water resulting from each liter of biofuel generated by different types of feedstock. The white background color indicates zero gray water because of the lack of crop data. Notably, regional nutrient-loading studies are less often available in the southwestern U.S., including California and the southern part of the Mountain region. The gray-water analysis results, therefore, are less representative in these states.

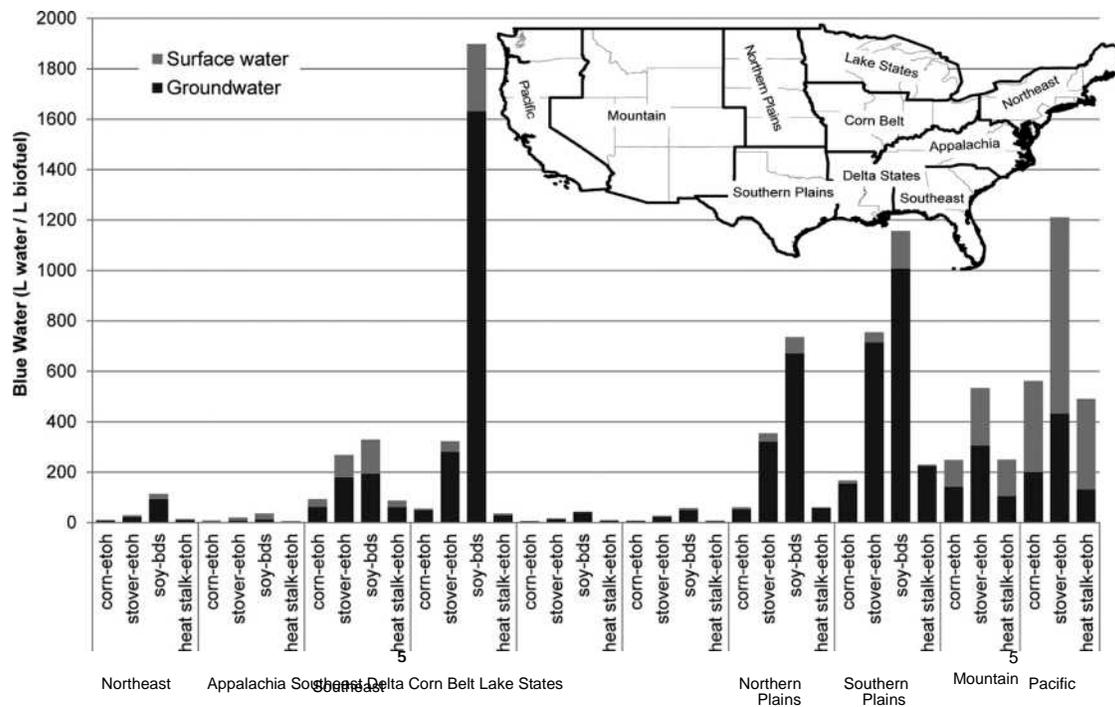


Figure 4. Regional blue-water footprint of biofuels from surface water and groundwater estimated from this study.

the Southeast regions are found to have larger gray-water footprints associated with biofuels. Figure 3 indicates that using the same feedstock acquisition assumptions as that in the previous section, the entire biofuel industry would result in total gray-water amounts ranging from 0.1 to 126 mm per square meter of cropland devoted to biofuel production. Corn-stover ethanol produced in the Delta region results in the highest gray-water footprint of 1508 L_w/L_{EtOH} , whereas soybean biodiesel from the same region show the lowest gray-water footprint of 30 L_w/L_{bds} .

3.4. Water-Resource Appropriation. Assuming the biofuel industry accounts for 30%,^{41,45} 24%,³² 12%,⁵ and 30% of corn, corn stover, soybeans, and wheat straws, respectively, as a norm, a total of 62 billion L of ethanol and 1.8 billion L of biodiesel can be produced. The total blue and green water volumes appropriated by the production of this magnitude of

biofuels range from merely a trace to 21% of the annual county-level effective precipitation. The highest appropriation occurs in the Northern Plains region (Figure 2).

We further analyze biofuel water footprint from the water-source aspects. The results indicate that approximate 77%, 85%, and 88% of the blue water consumed by corn-grain, corn-stover, and soybean biofuels production is sourced from groundwater, whereas 58% of wheat-straw bioethanol blue water is from groundwater (Figure 4). To produce a total of 63.8 billion L of biofuel using the prefixed amount of feedstocks as stated at the beginning of this section, the groundwater would contribute to the biofuel blue water from merely a trace to 3050 L_w/L_{bf} on the county level, and surface water would account for up to 3385 L of blue water in each liter of biofuel production depending on the location of a county. The local values are much higher than the national average of 67 L of

groundwater and 19 L of surface water per liter of biofuel. In general, the Southern Plain, Pacific, and Delta regions appear to source more groundwater than other regions on the per-liter biofuel basis (Figure 4).

3.5. Sensitivity Analysis. The perturbation method is employed to test the sensitivity of 13 selected entities in affecting the national average water footprint in liters of water per liter biofuel, including assumptions associated with crop yield, residue removal rates, process water, biofuel yield, fertilizer application rates, the fraction of nitrogen loading in fertilizer input, background nitrogen concentration, solar radiation, precipitation, temperature, and irrigation area (SI Figure S3).

We select corn stover as an example as the overall modeling structure of each biofuel feedstock pathway is similar. The results are obtained by increasing the examined factors independently by 1%, and indicate that blue, green, and gray water is highly affected by the ethanol yield. Individually, blue water is also sensible to the assumption of corn yield, whereas green water is very sensitive to the data accuracy of precipitation, and gray water is highly affected by the assumption of nitrogen fertilizer input and loading (SI Figure S3).

The results imply the importance of technology advancement in crop and fuel production, the monitoring of crop management data, and precision of precipitation data in estimating biofuel water footprint. This again echoes with the specific aims of this study that water footprint analysis must be conducted with a spatial resolution fine enough to reflect local climate and agricultural characteristics.

4. DISCUSSION

4.1. Data and Method Improvements. The estimates of the biofuel water footprints highly rely on the availability of input data, the interpretation of the production systems, and the assumptions of coproduct credits. Therefore, comparison of results among different studies must be made cautiously by clarifying data baselines, model resolutions, and production assumptions.

Comparing the water footprint of corn-grain ethanol and soybean biodiesel with the data compiled from a previous study of Mekonnen et al.,¹⁹ our results appear to be much lower. For example, Mekonnen et al. report a state-level blue water in corn-grain ethanol ranging from 0.1 L_w/L_{EtOH} to 1407 with a national average of 148 L_w/L_{EtOH} in the U.S., whereas we find blue water footprint of corn-grain ethanol ranging between 3 to 739 L_w/L_{EtOH} at the state level with a national average of 31 L_w/L_{EtOH} . However, the prior one applies a single-production system, where corn residue is not used as a product, and our study adopts a multiple-production system where both grain and a fraction of residue are harvested for fuels. To simulate a comparable corn ethanol—water footprint scheme, the portion of water footprint previous allocated to stover should then be accounted for the corn-grain ethanol if stover is not harvested for fuel, resulting in a 48% and 79% less green and blue water than what is estimated by Mekonnen et al. The difference between these values are anticipated and can be attributable to climate data year difference (1970—2000 in this study vs 1900—2002 in Mekonnen et al.), corn yield (1998—2008 in this study vs 2002 in Mekonnen et al.), irrigation estimates, and most importantly, the assumption of coproduct water allocation stated in methodology (SI). In terms of gray water, the results from our study are 33% and 126% higher in corn ethanol and

soybean biodiesel than what are estimated by Mekonnen et al.,¹⁹ comparing 548 L_w/L_{EtOH} and 115 L_w/L_{dsl} from our estimation with 412 L_w/L_{EtOH} and 51 L_w/L_{dsl} in Mekonnen et al. if stover is not removed for ethanol production. The results show that using local fertilizer input, watershed nutrient loading estimated by hydrological models calibrated by monitoring data, and watershed background nitrogen concentrations in this study can reshape the gray-water assessment. To determine the uncertainty in computing gray water, we compare the nitrogen loading and fertilizer application data derived from different hydrological models (SWAT vs SPARROW) using the Upper Mississippi River Basin as an example (SI Section 5). The estimation of gray water still remains as a challenge in water footprint accounting as SPARROW appears to be less sensitive to local soil, climate and hydrology characteristics than SWAT. However, SPARROW is the only available model that simulates nutrient transportation with national coverage with land use classifications. Although SWAT provides sophisticated simulation on nutrient fate and is preferred in quantifying nitrogen loading, its application on large geographical coverage requires tremendous efforts in computation. Therefore, the gray water footprint can only be interpreted as a reference for comparison instead of a validated value.

Coproduct credit is another key issue in water footprint accounting especially in the corn-ethanol system. Results indicate that without incorporating coproduct water credit, the total water footprints of the corn-grain ethanol is almost three times higher than those estimated with coproduct credits. Thus, the lack of considering coproduct credits can eventually lead to the overestimated biofuel water footprints. In addition, the relative lower value of corn ethanol—water footprint could be caused by a larger coproduct DDGS water credit in which a majority is from blue and green water use in feedstock production.

4.2. Spatial-Resolution Effects. As Figure 1 clearly shows, blue, green, and gray water footprint appear to have wide variances of distribution depending on the spatial scales examined. By changing the resolution from the county level to the national level, the extreme values associated with different input parameters are then compromised. Using corn ethanol as an example, the county-level corn yield ranges from 1500 to 16 600 kg/ha in the U.S., whereas the regional yield ranges from 4200 to 9400 kg/ha with a national average of 9020 kg/ha. For the counties growing corn, the average irrigated area fraction ranks from 0 to 100% at the county level, whereas that at the regional level falls between 1% and 89% with a national average of 15%. During the growing season, the lowest corn irrigation requirement is estimated as 7 mm, whereas the highest is 772 mm at the county level, but the regional value ranks from 134 to 366 mm with a national average of 217 mm.

Therefore, with an increase in resolution from national average to state to county, the ranges of green, blue, and gray water embodied in each pathway are amplified. Projections made on the basis of national averages can underestimate or overestimate the impact at the county level (Figure 1). If only limited small-scale samples are available, then it is advisable to carefully choose areas with representative irrigation and climate conditions for determining national or large-scale water footprints. However, water footprints derived using this bottom-up approach should not be applied to other local cases unless they share similar agricultural and climate characteristics.

4.3. Site Selection. Even though the county-level or finer-resolution analysis is preferred in assessing water footprints, each level of spatial resolution can actually have a certain degree of unique utility. For instance, the county-level analysis can provide fundamental information to support national energy policies, derive a key picture of the energy-water nexus, and estimate impacts. Regional assessment is suitable for supporting industrial decision-making processes, and provides regional long-term planning and water sustainability guidelines related to energy development. County-basis water footprint analysis is particularly beneficial for community engagement, local water impact assessment, and biofuel refinery site selection.

Using the results compiled from this study, each region can prioritize biofuel feedstocks by comparing water demand and supply associated with various biofuel life cycles. As shown in Figure 2, regions of the Northeast, Appalachia, the Corn Belt, and the Lake States are suitable for multiple feedstock combinations, whereas the Southeast may choose corn ethanol and wheat-straw ethanol over other pathways. The Delta and the Northern Plains regions may promote wheat-straw ethanol in response to blue-water assessment results.

4.4. Sustaining Water Resources. Traditional perspectives in defining biofuel sustainability are often found to be driven by economic and infrastructure considerations⁴⁶⁻⁴⁹ or, to some extent, by ecological and environmental quality related to land resources.^{50,51} Our study quantifies biofuel water footprints on the county level, taking water resource limitations into account, and can facilitate the consideration of supplementary factors in defining sustainable biofuels.

If the feedstock acquisition scenario described in the Results section (see “Water-Resource Appropriation by Region”) is followed, then biofuel blue and green water together can account for 1.5% of the national annual effective precipitation, in which over 84% of the counties in the U.S. appropriate less than 5% of local annual effective precipitation for biofuels production. The Northern and Southern Plains regions sourced 91% of their blue water from groundwater (Figure 4), which is supported by the nation's largest fossil water reservoir, the Ogallala Aquifer. The variation of water resource dependency indicates that the water requirement for biofuels remains as a local challenge.

Future refinery site selection and biofuel production scenarios combining multiple feedstock pathways can be further assessed using the water footprint developed in this study. By quantifying water requirements on a county basis and disaggregating green, blue, and gray water compartments, we can better elucidate how biofuel policies will shape national and local water resources. Steps to prevent consequential impact can also be taken by adopting suitable site selection and suitable land screening based on the water demand and supply analysis.

■ ASSOCIATED CONTENT

[a Supporting Information

Blue, green, and gray water calculations; equations for converting ratios of nitrogen input and loading, assumptions and modeling; water allocation, coproduct credits; refinery process water consumption; and sensitivity analysis results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) U.S. Environmental Protection Agency, *Renewable fuel standard (RFS)*. Available at <http://www.epa.gov/otaq/faels/renewablefaels/> (accessed 11/21/2011).
- (2) Pingoud, K.; et al. Bioenergy: Counting on incentives. *Science* 2010, *327*(5970), 1199-1200.
- (3) Regalbutto, J. R. Cellulosic biofuels—Got gasoline? *Science* 2009, *325*(5942), 822-824.
- (4) Robert, D., et al. *Biomass As Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*; DOE and Oak Ridge National Laboratory: Oak Ridge, TN, 2005.
- (5) National Biodiesel Board, Biodiesel production estimates CY 2005 to 2010. Available at <http://www.biodiesel.org/resources/fuelfactsheets/default.shtm> (accessed 10/15/2011).
- (6) OECD-FAO, *Agricultural Outlook 2011-2020, Chapter 3: Biofuels*; OECD-FAO: Paris, France, 2011; p 19.
- (7) Hoogeveen, J.; Faures, J.-M.; van de Giessen, N. Increased biofuel production in the coming decade: To what extent will it affect global freshwater resources? *Irrigation Drainage* 2009, *58*(S1), S148-S160.
- (8) Wu, M.; Chiu, Y.-W.; Demissie, Y. Quantifying the regional water footprint of biofuel production by incorporating hydrologic modeling. *Water Resour. Res.* 2012, under review.
- (9) King, C. W.; Webber, M. E. Water intensity of transportation. *Environ. Sci. Technol.* 2008, *42*(21), 7866-7872.
- (10) Chiu, Y.; Walseth, B.; Suh, S. Water embodied in bioethanol in the United States. *Environ. Sci. Technol.* 2009, *43*(8), 2688-2692.
- (11) Gerbens-Leenes, W.; Hoekstra, A. Y.; van der Meer, T. H. The water footprint of bioenergy. *Proc. Natl. Acad. Sci.* 2009, *106*(25), 10219-10223.
- (12) Mishra, G. S.; Yeh, S. Life cycle water consumption and withdrawal requirements of ethanol from corn grain and residues. *Environ. Sci. Technol.* 2011, *45*(10), 4563-4569.
- (13) Wu, M.; Mintz, M.; Wang, M.; Arora, S. Water consumption in the production of ethanol and petroleum gasoline. *Environ. Manage.* 2009, *44*(5), 981-997.
- (14) Gerbens-Leenes, P. W.; Hoekstra, A. Y. *the Water Footprint of Sweeteners and Bio-Ethanol from Sugar Cane, Sugar Beet and Maize*; UNESCO-IHE Institute for Water Education: Delft, Netherlands, 2009.
- (15) Scown, C. D.; Horvath, A.; McKone, T. E. Water footprint of U.S. transportation fuels. *Environ. Sci. Technol.* 2011, *45*(7), 2541-2553.
- (16) Evans, J. M.; Cohen, M. J. Regional water resource implications of bioethanol production in the southeastern United States. *Global Change Biol.* 2009, *15*(9), 2261-2273.
- (17) Wu, M., et al. *Consumptive Water Use in the Production of Ethanol and Petroleum Gasoline - 2011 Update*; ANL/ESD/09-1 update; Argonne National Laboratory, Lemont, IL, July, 2011.
- (18) Lienden van, A. R.; Gerbens-Leenes, P. W.; Hoekstra, A. Y.; van der Meer, T. H. Biofuel scenarios in a water perspective: The global blue and green water footprint of road transport in 2030. UNESCO-IHE Institute for Water Education: Delft, Netherlands, 2010.
- (19) Mekonnen, M.; Hoekstra, A. The green, blue and grey water footprint of crops and derived crop products. *Hydrol. Earth System Sci.* 2011, *15*, 1577-1600.
- (20) Goolsby, D. A., et al. *Flux and Sources of Nutrients in the Mississippi-Atchafalaya River Basin*; NOAA Coastal Ocean Program

- Decision Analysis Series No. 17; NOAA Coastal Ocean Program: Silver Spring, MD, 1999.
- (21) Hoekstra, A. Y.; Chapagain, A. K.; Aldaya, M. M.; Mekonnen, M. M. *the Water Footprint Assessment Manual: Setting the Global Standard*; Earthscan: London, UK, 2011.
- (22) U.S. Geological Survey, Water use in the United States 1985, 1990, and 1995. Available at <http://water.usgs.gov/watuse/> (accessed 05/20/2011).
- (23) U.S. Department of Agriculture, *1998 Farm and Ranch Irrigation*; USDA: Washington, DC, 1999.
- (24) U.S. Department of Agriculture, *2003 Farm and Ranch Irrigation*; USDA: Washington, DC, 2004.
- (25) U.S. Department of Agriculture, *2008 Farm and Ranch Irrigation*; USDA: Washington, DC, 2009.
- (26) Mueller, S. 2008 National dry mill corn ethanol survey. *Biotechnol. Lett.* 2010, *32* (9), 1261-1264.
- (27) Argonne National Laboratory, The greenhouse gases, regulated emissions, and energy use in transportation model(GREET). Available at <http://greet.es.anl.gov/> (accessed 11/20/2011).
- (28) Agricultural Research Service USDA, *Soybean Biodiesel ASPEN Model*; USDA: Washington, DC, 2011.
- (29) Mekonnen, M.; Hoekstra, A. A global and high-resolution assessment of the green, blue and grey water footprint of wheat. *Hydrol. Earth System Sci* 2010, *14*, 1259-1276.
- (30) Economic Research Service of USDA, Fertilizer use—Corn, soybeans, and wheat. Available at <http://www.ers.usda.gov/Data/FertilizerUse/> (accessed 08/15/2011).
- (31) Demissie, Y.; Zhang, Z.; Wu, M.; Yan, E. Developing a watershed model for evaluation of biofuel feedstock production in the upper Mississippi river basin. *J. Hydrol. Proc.* 2010.
- (32) Wu, M.; Demissie, Y.; Yan, E. Simulated impact of future biofuel production on water quality and water cycle dynamics in the upper Mississippi river basin. *Biomass Bioenergy* 2012, *41*, 45-56.
- (33) U.S. Geological Survey, Total nitrogen model for the great lakes, ohio, upper Mississippi, and souris-red-rainy region-2002. Available at <http://cida.usgs.gov/sparrow/#modelid=22> (accessed 11/15/2011).
- (34) U.S. Geological Survey, Total nitrogen model for the lower Mississippi, arkansas-white-red, and texas-gulf region-2002. Available at <http://cida.usgs.gov/sparrow/#modelid=22> (accessed 11/15/2011).
- (35) U.S. Geological Survey, Total nitrogen model for the missouri river basin-2002. Available at <http://cida.usgs.gov/sparrow/#modelid=22> (accessed 11/15/2011).
- (36) U.S. Geological Survey, Total nitrogen model for the new england and mid-atlantic region-2002. Available at <http://cida.usgs.gov/sparrow/#modelid=22> (accessed 11/15/2011).
- (37) U.S. Geological Survey, Total nitrogen model for the pacific northwest-2002. Available at <http://cida.usgs.gov/sparrow/#modelid=22> (accessed 11/15/2011).
- (38) U.S. Geological Survey, Total nitrogen model for the south atlantic-gulf and tennessee region-2002. Available at <http://cida.usgs.gov/sparrow/#modelid=22> (accessed 11/15/2011).
- (39) U.S. Geological Survey, Estimated use of water in the United States county-level data for 2005. Available at <http://water.usgs.gov/watuse/data/2005/> (accessed 10/06/2010).
- (40) National Climate Data Center, 1971-2000 U.S. climate normals products: Clim 84 daily normals. Available at <http://www.ncdc.noaa.gov>.
- (41) U.S. Department of Agriculture, National agricultural statistics service. Available at <http://www.nass.usda.gov/> (accessed 04/20/2010).
- (42) U.S. Department of Agriculture, *1997 Census of Agriculture*; USDA: Washington, DC, 1999.
- (43) U.S. Department of Agriculture, *2002 Census of Agriculture*; USDA: Washington, DC, 2004.
- (44) U.S. Department of Agriculture, *2007 Census of Agriculture*; USDA: Washington, DC, 2009.
- (45) Renewable Fuels Association, Ethanol biorefinery statistics. Available at <http://www.ethanolrfa.org/> (accessed 01/10/2009).
- (46) Ayhan, D. Political, economic and environmental impacts of biofuels: A review. *Appl Energy* 2009, *86* (Supplement 1 (0)), S108-S117.
- (47) Gutierrez, A. P.; Ponti, L. Bioeconomic sustainability of cellulosic biofuel production on marginal lands. *Bull. Sci., Technol Soc.* 2009, *29* (3), 213-225.
- (48) Jacobson, J. J., et al. *Sustainable Biomass Supply Systems*; Idaho National Laboratory: Idaho Falls, ID, 2009.
- (49) Richard, T. L. Challenges in scaling up biofuels infrastructure. *Science* 2010, *329* (5993), 793-796.
- (50) Hecht, A.; et al. Good policy follows good science: Using criteria and indicators for assessing sustainable biofuel production. *Ecotoxicology* 2009, *18* (1), 1-4.
- (51) Dragisic, C.; et al. Tools and methodologies to support more sustainable biofuel feedstock production. *J. Ind. Microbiol. Biotechnol.* 2011, *28* (2), 271-274.