

Quantifying the regional water footprint of biofuel production by incorporating hydrologic modeling

M. Wu,¹ Y. Chiu,¹ and Y. Demissie²

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[1] A spatially explicit life cycle water analysis framework is proposed, in which a standardized water footprint methodology is coupled with hydrologic modeling to assess blue water, green water (rainfall), and agricultural grey water discharge in the production of biofuel feedstock at county-level resolution. Grey water is simulated via SWAT, a watershed model. Evapotranspiration (ET) estimates generated with the Penman-Monteith equation and crop parameters were verified by using remote sensing results, a satellite-imagery-derived data set, and other field measurements. Crop irrigation survey data are used to corroborate the estimate of irrigation ET. An application of the concept is presented in a case study for corn-stover-based ethanol grown in Iowa (United States) within the Upper Mississippi River basin. Results show vast spatial variations in the water footprint of stover ethanol from county to county. Producing 1 L of ethanol from corn stover growing in the Iowa counties studied requires from 4.6 to 13.1 L of blue water (with an average of 5.4 L), a majority (86%) of which is consumed in the biorefinery. The county-level green water (rainfall) footprint ranges from 760 to 1000 L L⁻¹. The grey water footprint varies considerably, ranging from 44 to 1579 L, a 35-fold difference, with a county average of 518 L. This framework can be a useful tool for watershed- or county-level biofuel sustainability metric analysis to address the heterogeneity of the water footprint for biofuels.

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1. Introduction

[2] Biofuel production has been increasing as a result of policy for energy security, environmental benefits, and an improved rural economy. In 2010, global biofuel production increased by 17% and reached an all-time high of 105 billion liters, driven by a combination of factors, such as high oil prices, a global economic rebound, and new laws and mandates in several countries. The United States produced 49 billion liters of ethanol, mainly from starch feedstock, accounting for 47% of the world total. Cellulosic-based biofuel is projected to increase, with an estimated one billion short tons of feedstock becoming available by 2030 [*U.S. Department of Energy*, 2011]. Other biofuel resources have also been explored [*Wigmosta et al.*, 2011]. In this context, the water-bioenergy nexus is increasingly important. Because water resources vary regionally and water use in biofuel production is feedstock and technology dependent, it is vital to address the impacts of biofuel production on water resources with spatial resolution [*Phong et al.*, 2011; *Georgescu et al.*, 2011] and across the product

life cycle. Doing so will improve our understanding of the complexity of the energy-water nexus, identify critical issues in the biofuel supply chain as they relate to water quantity and water quality, and support the planning of sustainable biofuel production.

[3] Conceptually, the biofuel water footprint during the crop growing and refinery conversion stages can be partitioned into three compartments, including green water, blue water, and grey water (Figure 1). Green water represents rainwater used to support crop growth through evapotranspiration (ET); blue water represents surface water and groundwater use by crop through ET and in the production of fuels, energy, and other goods. Grey water is defined as the volume of freshwater that is required to assimilate the load of nutrients/chemicals on the basis of water quality standards established by the U.S. Environmental Protection Agency (EPA). *Chapagain and Hoekstra* [2004] proposed a water footprint accounting methodology for products, countries, and regions. The method is currently being incorporated into an ISO standard (http://www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=43263). Historically, a number of studies have attempted to estimate biofuel water requirements across the major stages of the biofuel supply chain [*Mishra and Yeh*, 2011; *Scown et al.*, 2011; *Wu et al.*, 2009, 2011; *Gerbens-Leenes et al.*, 2009; *Gerbens-Leenes and Hoekstra*, 2009; *Chiu et al.*, 2009; *Evans and Cohen*, 2009; *King and Webber*, 2008]. The feedstock analyzed by these researchers includes grain, sugar crops, agricultural residue, herbaceous grass, and forest wood. Although the studies share a similar objective of

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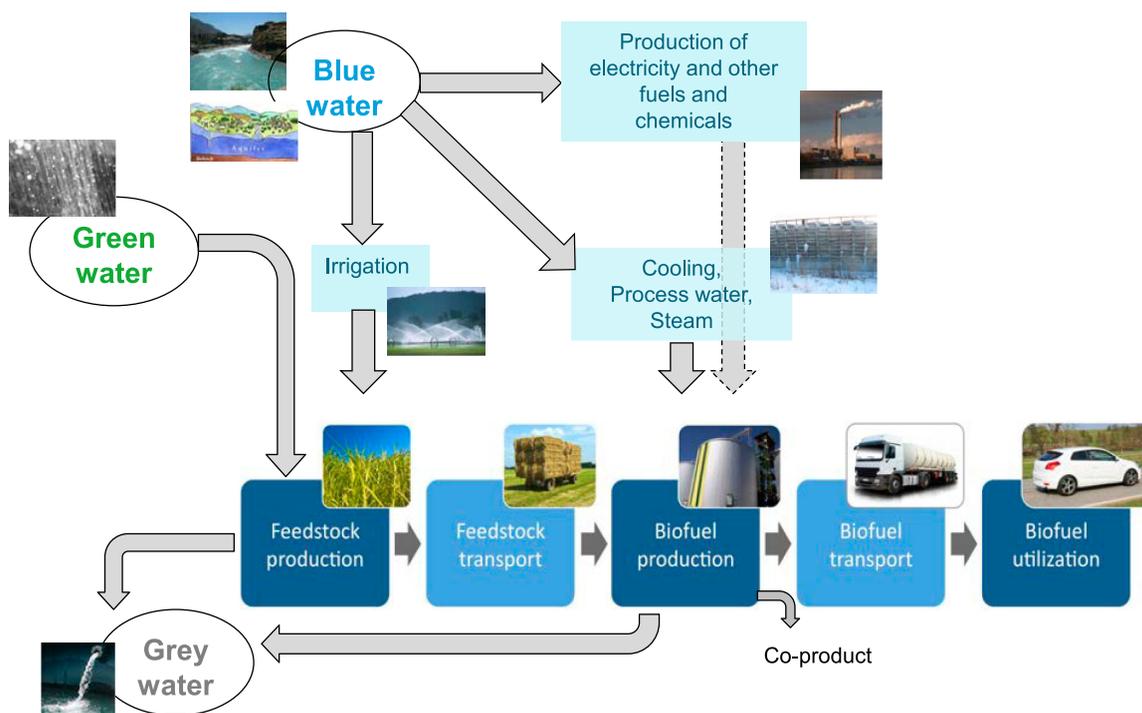


Figure 1. Schematic representation of the system boundary for the biofuel water footprint analysis.

quantifying the biofuel water footprint, they show vastly wide variations of results because of differences in terms of scale, system boundaries, analysis matrices, assumptions, and methodologies.

[4] Several studies focus on irrigation water withdrawal [Chiu *et al.*, 2009; Scown *et al.*, 2011; Evans and Cohen, 2009], while others examine consumptive irrigation water use for crops [Gerbens-Leenes *et al.*, 2009; Mishra and Yeh, 2011; King and Webber, 2008; Wu *et al.*, 2009, 2011; Gerbens-Leenes and Hoekstra, 2009], which excludes the portion of irrigation water that is returned to the resource. In a recent publication, Mishra and Yeh [2011] include both water withdrawal and consumption assessments. That work provides a detailed examination of the water transport and delivery process in California in the United States, where water loss in the process is a key factor in the overall water consumption of the state. Few studies examined both blue and green water use [Gerbens-Leenes *et al.*, 2009; Evans and Cohen, 2009; Mishra and Yeh, 2011].

[5] Embedded water use for the production of biofuel is addressed in several analyses [King and Webber, 2008; Scown *et al.*, 2011] for a full life cycle assessment (LCA). Refinery coproduct water use allocation has been considered for corn ethanol [King and Webber, 2008; Gerbens-Leenes and Hoekstra, 2009; Scown *et al.*, 2011; Wu *et al.*, 2011], cellulosic ethanol [Scown *et al.*, 2011], and sugar cane and sugar beet ethanol [Gerbens-Leenes and Hoekstra, 2009]. Water allocation between the grain and residue feedstocks has been considered in two studies [King and Webber, 2008; Gerbens-Leenes *et al.*, 2009]. Grey water is covered only in two analyses by Gerbens-Leenes and Hoekstra [2009] and Evans and Cohen [2009]. As a result of the fundamental differences in approach described above, the estimated water use per liter of biofuel production varies significantly (even for one specific biofuel produced from a

similar region), making it difficult to compare the water footprint estimate among these studies.

[6] Another source of uncertainty is from estimates of ET. Historically, water vapor transfer methods have been used to conduct field- or plot-scale in situ measurements of ET (such as Eddy covariance, Bowen ratio) and components of evaporation (such as soil evaporation, rainfall interception loss, sap flow). Alternatively, water budget measurements (such as soil moisture depletion, evaporation pan) are often used [Schilling, 2007; Logsdon *et al.*, 2009]. For regional- and landscape-scale measurements, large-scale measurements of evaporation (such as remote sensing and more recently satellite imagery) are frequently performed, which offer broad spatial and temporal coverage [Bastiaansen *et al.*, 1998a, 1998b; Allen *et al.*, 2011; Zhang *et al.*, 2010]. However, in the life cycle water analysis, water footprint accounting relies on Penman-Monteith method to estimate reference ET and couple it with crop parameters to derive crop ET. Validation of ET was rarely performed. Nevertheless, recent work began to explore the potential of using remote sensing techniques for estimating the water footprint of crops [Romaguera *et al.*, 2010]. How well the estimated ET in water footprint represents field conditions across various regions has not been fully addressed. In addition, current water footprint analyses are based mostly on high-level political boundaries (e.g., country or state) such that spatial variations within a state are not explicitly represented.

[7] The key gap in water footprint analyses exists in grey water. Its evaluation rarely considers hydrogeologic conditions, which play a key role in water resource and water quality. For example, nitrogen loading, a key component in grey water, was, for the most part, estimated by assigning a fixed fraction of fertilizer applied to the crop for the entire analyzed area, which may underestimate or overestimate the loadings caused by fertilizer use in different geological

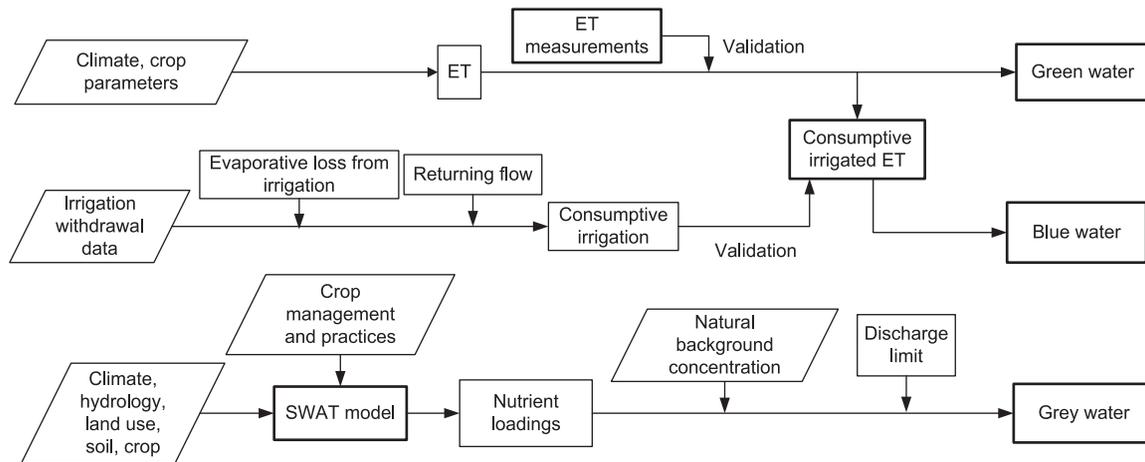


Figure 2. Analytical framework for estimating green, blue, and grey water footprint of biofuels in the feedstock production stage. The hydrologic model SWAT is used to simulate agricultural grey water.

areas [Chiu and Wu, 2012]. As in LCA and other analysis areas, data monitoring and availability presents a challenge to water foot printing, especially for agricultural grey water, either not available or not measured systematically over long periods across various locations. Watershed modeling to simulate grey water would be one option to address this issue.

[8] This study seeks to develop an integrated analytical framework to quantify the water footprint of conventional, cellulosic, and advanced biofuel with spatial resolution at the county level. The primary objectives are to establish a water footprint of green, blue, and grey water for biofuel by incorporating hydrological modeling into the water footprint methodology. Another objective of this work is to refine the estimates of ET and the blue water use by verifying them against field data. Our intent is to include spatial variability and fill the grey water data gap in the analysis through consideration of watershed climate, hydrological, and soil conditions, thereby improving the fidelity of the water footprint analysis.

2. Methods

[9] The system boundary of water footprint covers feedstock production, feedstock preparation and transport, and feedstock conversion in biorefinery (Figure 1). Note that the blue and grey water use has occurred throughout the entire production life cycle, while green water use is only limited to the feedstock production.

2.1. Consumptive Use of Green and Blue Water

2.1.1. Consumptive Green and Blue Water Use in Feedstock Production

[10] Figure 2 presents the analytical framework developed in this study for estimating the green, blue, and grey water footprint of biofuels in the feedstock production stage. Both feedstock green water and blue water are estimated through crop ET, which indicates the crop's water demand that is satisfied by irrigation (blue) and rain-fed water (green). Several steps are taken for green water and blue water calculations (Figure 2). Consumptive green water for feedstock is computed from effective rainfall, while consumptive blue water is estimated from the differential of ET

and effective rainfall. The resultant consumptive blue water is then verified against irrigation survey data by adjusting an irrigated area factor at the county level.

[11] The effective rainfall P_{eff} is obtained by applying the definition and method proposed by the U.S. Department of Agriculture (USDA) Natural Resources Conservation Service (NRCS) [Kent, 1972; NRCS, 1997], which accounts only for precipitation available for crop consumptive use. It is assumed that there is no further runoff or deep percolation of the precipitation after an effective rainfall.

[12] A reference ET (ET_o) was estimated by using the Penman-Monteith equation [Allen et al., 1998]. A set of monthly crop coefficients K_c for each crop over the entire growing season was collected from the literature. Crop ET was calculated from the ET_o and K_c at each location. The calculated ET values were further verified with measurements gathered by field instrumentation and remote sensing, as well as on the basis of values derived from satellite imagery data for this area. The monthly crop-specific ET value is summed to annual ET, together with the effective rain and crop-harvested area, to obtain the green and initial blue water use. Detailed calculations equations of consumptive green and blue water are presented in the auxiliary material.¹

[13] The calculated crop blue water requirement is verified with irrigation survey data. The volume of actual annual consumptive irrigation is calculated on the basis of the crop-specific state-level irrigation withdrawal data survey reported in the Farm and Ranch Irrigation Survey (FRIS) by the USDA [2003, 2008] and the irrigation returning flow for each state estimated by the U.S. Geological Survey (USGS; Water use in the United States for years 1985, 1990, 1995, <http://water.usgs.gov/watuse/>, accessed September 2011). The differential between the total irrigation water withdrawal and the irrigation returning flow contributes to consumptive crop irrigation, which includes water used by the crop through ET and water losses through conveyors and irrigation application equipment. As presented in Figure 2, the actual consumptive irrigation derived from USGS and

¹Auxiliary materials are available in the HTML. doi:10.1029/2011WR011809.

USDA data were compared with the calculated initial estimate of consumptive irrigated ET (ET_{IRG}). By using a water balance, a state-level calibration factor f_{cb} has been determined (equation (1)). Of the irrigation water lost through the conveyance and irrigation application, generally between 0.12% and 2.5% of the total water loss is evaporative [Mishra and Yeh, 2011]. The nonevaporative loss during the conveyance and irrigation application eventually returns to the hydrosystem through surface runoff and soil percolation to shallow groundwater and becomes part of the returning flow RF in equation (1).

$$IRGw - L_{IRG} - L_{CV} - RF = ET_{IRG} \times f_{cb} = BWc \quad (1)$$

where IRGw is the reported irrigation withdrawal volume (L), RF is the irrigation flow returning to the water body (L), L_{IRG} is the evaporative water loss from irrigation application (L), L_{CV} is the evaporative water losses from conveyance (L), f_{cb} is the state-level calibration factor (unitless), and BWc is the blue water consumption (L).

2.1.2. Blue Water Use in Feedstock Transport and Refinery Conversion

[14] Feedstock is harvested and stored before shipment to the biorefinery. Grains are stored in silos, and agricultural residue and perennial grass are baled and field dried. During the process, the water requirement is nearly zero. In a biorefinery, feedstock is converted to biofuel via biochemical, thermochemical, or physical chemical processes. At present, a majority of corn ethanol plants built in the Midwest source groundwater because of its consistent quality. Process water consumption is primarily from cooling and heating requirements and varies with feedstock conversion technologies employed for biofuel production [Wu et al., 2009]. Generally, water use in a biorefinery for producing conventional biofuel from starch (e.g., corn, wheat, sorghum) and oil seeds (e.g., soybeans) is well documented [Keeney and Muller, 2006; Keeney, 2007; Pradhan et al., 2011; Wu et al., 2009]. Cellulosic biofuels, however, are still in the early development stage; therefore, water figures associated with large-scale production are lacking. Using ASPEN Plus process simulation tool, Humbird et al. [2011] reported that 5.4 L of water is required to produce one liter of cellulosic ethanol from corn stover and switch grass via a biochemical process at an ethanol yield of 329.5 L per dry metric ton (DMT). Fuel blending and transportation to a refueling station consumes minimal water and was therefore not included in this study.

2.2. Grey Water

[15] Grey water is defined as the volume of freshwater that is required to assimilate the load of nutrients/chemicals on the basis of water quality standards established by the U.S. Environmental Protection Agency (EPA) safe drinking water standard in 1997 (<http://water.epa.gov/drink/contaminants/basicinformation/nitrate.cfm#four>). Several common chemicals are released from the biofuel supply chains, such as nitrogen, phosphorus, potassium, and lime, that result from fertilizer application during feedstock cultivation; others are from the refinery, such as ammonia and sulfuric acid in biochemical conversion [Humbird et al., 2011]. Ammonia content in the refinery treated wastewater is practically nil as almost all of it goes to the brine and sludge, according to

process simulation by Humbird et al. [2011]. Nitrogen in the feedstock production stage is the dominant nutrient that accounts for a majority of the grey water because of the large amount required for application. Among the nitrogen compounds discharged, nitrate is extensively monitored and tightly regulated by the U.S. EPA because of its water solubility and resultant detrimental health effects to infants. This study focuses on nitrogen and phosphorus. Nutrient loadings (nitrogen and phosphorus) were simulated by using a SWAT model [Neitsch et al., 2002]. Grey water was determined in accordance with Hoekstra et al. [2011]. Equation (2) presents the nitrate grey water calculation, which characterizes the relative proportion of the actual nitrogen input in the region (L_{NO_3}) to the allowable nitrogen level increase ($NO_{3\text{permit}} - C_{NO_3}$). The allowable nitrogen level increase reflects the capacity of the ecosystem in the region to assimilate nitrate loadings.

$$GyW = \frac{L_{NO_3}}{NO_{3\text{permit}} - C_{NO_3}} \quad (2)$$

where GyW is nitrate grey water (m^3), L_{NO_3} is the nitrate loading ($kg\ yr^{-1}$) in water bodies as a result of nitrogen inputs, $NO_{3\text{permit}}$ is the nitrate concentration in ambient water quality standards set by the EPA ($10\ kg\ m^{-3}$), and C_{NO_3} is the natural background nitrate concentration in the water stream in the region ($kg\ m^{-3}$).

[16] Phosphorus grey water is determined in a similar fashion. Nitrate is the largest component in the grey water because its loading far exceeds that of phosphorus. Thus, the resulting estimate of nitrate grey water volume also includes that of phosphorus. Similar to green and blue water, grey water during feedstock transport is negligible.

2.3. Application of the Framework: A Case Study

[17] To illustrate the method, a case study is presented in which the water footprint of cellulosic biofuels produced from corn stover was estimated for the counties of Iowa residing in the Upper Mississippi River basin in the United States (Figure 3). Iowa is ranked as the number one corn grower in the United States and is potentially the largest corn-stover-derived ethanol producer. The water footprint is estimated for a biorefinery located in Iowa, operating at 2000 dry metric tons per day (DMT d^{-1}) by 2017. Stover is harvested at 24% of total production. The Iowa-grown corn stover is converted to ethanol via a biochemical process with dilute acid pretreatment and enzymatic hydrolysis. The process would generate 330 L ethanol/DMT of stover and use 5.4 L of process water for each liter of ethanol produced, on the basis of an ASPEN plus process simulation [Humbird et al., 2011]. Water use figures presented here account for the net water use, which includes process water recycling.

[18] Nitrate grey water is analyzed in this case study since the region is primarily an agriculture area and corn is the dominant crop. The input data ranges for the case are presented in Table 1. Feedstock harvest scheme, irrigation requirement, and blue and green water are presented in Table S1 in the auxiliary material; monthly K_c values are listed in Table S2.

2.3.1. SWAT Modeling

[19] A SWAT model application for the Upper Mississippi River basin (UMRB) at an eight-digit HUC watershed

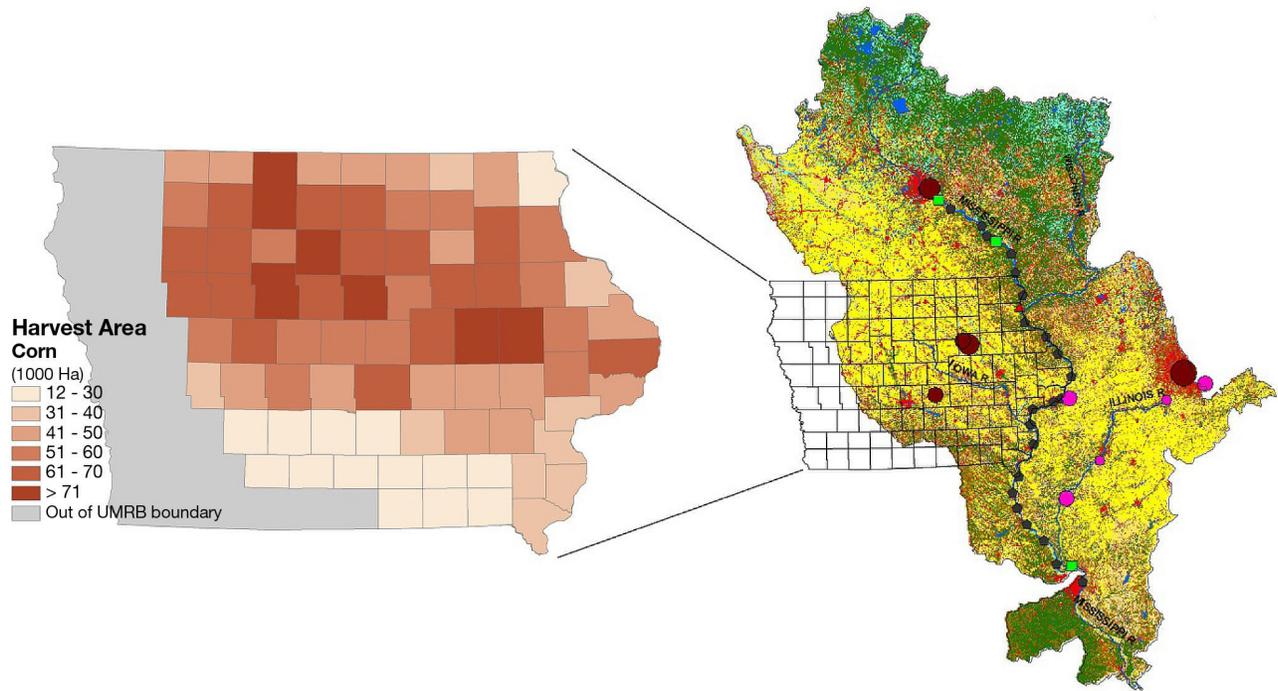


Figure 3. Corn land area by county in the state of Iowa for the stover harvest case and its location in the Upper Mississippi River Basin in the United States. Latitude ranges from 37.28°N to 47.42°N; longitude ranges from 87.07°W to 96.67°W.

scale was developed by *Demissie et al.* [2012] to simulate nitrogen/nitrate loadings for Iowa counties that reside in the UMRB (Figure 3). Twenty year climate data, soil information, and crop management information and practices were incorporated into the model to simulate crop growth through water balance, nitrogen and phosphorus cycles, and carbon balance. Fertilizer application in the SWAT baseline model was simulated on the basis of nutrient requirements during the crop-growing season. A future scenario was developed by using SWAT to simulate partial corn stover removal (24%) for 2017 [*Wu et al.*, 2012]. Future crop yield was projected and fertilizer application rate was simulated by SWAT incorporating 30 year historical trends of fertilizer application rates [*Wu et al.*, 2012]. Supplemental nitrogen fertilizer was applied to the field where stover was removed to compensate for the nutrient

loss due to the stover harvest. Resultant subbasin level (HUC-8) nutrient loadings from the SWAT simulation were converted into a county basis by using the zonal statistic function in ArcGIS. The county-level natural background concentration of nitrate, nitrate loading, and grey water estimate for the areas analyzed are presented in Table S3.

2.3.2. Upstream Feedstock Input Allocation

[20] Historically, it has been a conservation practice that when corn grain is harvested, the stover is left in the field for a majority of the corn-growing areas. The stover plays a role in providing ground cover, adding carbon and nutrients to the soil while excess stover can be used as feedstock. In this study, corn grain and residue (stover) can both serve as feedstock for biofuels. Therefore, corn grain and harvested stover would appropriate a fraction of blue water and green water associated with the corn growth. Similar to energy and GHG LCA, where upstream input to produce feedstock is allocated on the basis of mass (EcoInventory, <http://www.netgen.co.za/portfolio/ecoinventory-software/>, and GREET, <http://greet.es.anl.gov/publications>), water use for corn growth is shared between corn grain and harvested corn stover. Thus, the blue water and green water are first partitioned between grain and stover according to their mass ratio, which is 1:1 (grain to stover) at maturity [*White and Johnson*, 2003]. Since only a fraction of stover is harvested (24% of the stover, or 12% of total aboveground biomass), grain and harvested stover initially bear the water burden of 50% and 12%, respectively. The remaining fraction of blue and green water (38%) is further distributed among the grain and harvested stover on the basis of their mass fraction. When a portion of the corn stover is harvested, supplemental fertilizer would be required to compensate for the nutrient loss due to stover removal. Therefore, in grey water calculations, fertilizer input

Table 1. Summary of Major Inputs for Production of Feedstock and Biofuel

Parameter	Value
Corn harvest area ^a (ha)	11,952–119,666
Stover harvested ^b (DMT)	21,470–246,256
Nitrogen fertilizer applied ^c (kgN ha ⁻¹)	140–158
Stover harvested in total stover produced (%)	24
Ethanol yield in biorefinery (L ethanol/DMT)	330
Refinery blue water use ^d (L L ⁻¹ ethanol)	4.63

^aHarvested area at county level.
^bValue represents total stover harvested at county level. DMT denotes dry metric tons. The moisture content for stover is 15%.
^cValue represents the sum of fertilizer applied during the crop growth and supplemental fertilizer required to compensate for nutrient loss due to stover removal from the field.
^dNet water use, which is considered process water recycling.

to grow corn is allocated between grain and stover on the basis of mass fraction, while the supplemental fertilizer is allocated exclusively to stover.

2.3.3. Refinery Coproduct

[21] Biofuel production yields various coproducts, depending on the conversion processes in the biorefinery. These coproducts would share a water credit in the water footprint accounting. Methods dealing with coproduct in energy and emission LCA have been compared extensively for biofuel applications [Wang *et al.*, 2011]. For attributional LCA, ISO 14,040 (http://www.iso.org/iso/catalogue_detail?csnumber=37456) recommended the use of the system expansion method whenever possible in dealing with coproducts. Since this study focuses on the heterogeneity of the water footprint under the current context, which is appropriate for attributional LCA, we adopt the system expansion method for analyzing refinery coproduct. In the biochemical conversion process, the main coproduct would be bioelectricity; excess bioelectricity is generated for export at 1.8 kWh per gallon of ethanol produced from corn stover [Humbird *et al.*, 2011]. The bioelectricity would displace the electricity mix in Iowa. Blue water consumption for producing the electricity generation mix in Iowa is 0.5279 gal/kWh, as simulated from a power-water tool developed at Argonne National Laboratory [Wu and Peng, 2011]. The blue water credit associated with generating the displaced electricity is then determined.

2.3.4. Data Source

[22] All of the required climate data used in this study were derived from the National Climate Data Center of the NOAA for the period from 1970 to 2000. Agricultural data of crop-harvested acreage were acquired from USDA national statistics (National Agricultural Statistics Service, Agricultural data of yield and crop-harvested acreage, available at <http://www.nass.usda.gov/>, accessed January 2011; USDA Census of Agriculture, Agricultural data of crop irrigated acreage at county level, available at <http://www.agcensus.usda.gov/>, accessed January 2011). The crop coefficient K_c in estimating ET was compiled from the High Plains Regional Climate Center (http://www.hprcc.unl.edu/awdn/et/crop/crop_corn.txt, accessed February 2011), the Texas High Plains Evapotranspiration network [Marek *et al.*, 2006], and previous studies by Kiniry *et al.* [1999]. Irrigation withdrawal volume, state-level irrigated crop acreage data, and the evaporative loss from irrigation application and conveyance were collected from the 2003 and 2008 USDA Farm and Ranch Irrigation Survey [USDA, 2003, 2008]. County-level irrigated acreage data were not available from FRIS, but data for the preceding year were available from the U.S. Census. An assumption was made that, within a state, the distribution of irrigated acreage for a specific crop would remain the same in the following year (i.e., the relative proportion of the county-level irrigated acreage to the state total would remain unchanged). The irrigation flow returning to a water body was provided by USGS data for 1985–1995 (<http://water.usgs.gov/watuse>). The background nitrate concentration C_{NO_3} was derived from the 1976–1997 USGS data set [Smith *et al.*, 2003]. The data set accounts for total nitrogen concentration at the eight-digit HUC watershed scale. The C_{NO_3} was then determined by assuming a nitrate to total nitrogen ratio, $f_{\text{NO}_3\text{-TN}}$, and, therefore, a concentration ratio of 0.95, on the basis a watershed modeling study by Demissie *et al.* [2012].

3. Results and Discussions

3.1. ET Verification

[23] The estimated ET of corn during the growing season from this study agreed well, in general, with the values available in the literature and with the database obtained from soil moisture measurements, remote sensing data, and satellite-based estimates for the area studied. Schilling [2007] determined ET by using soil moisture measurements and reported ET values ranging from 4.1 (July 2004) to 1.3 mm d⁻¹ (August in 2004) at a cornfield in Jasper County, Iowa. Logsdon *et al.* [2009] reported the mean ET for corn as 4.0 and 5.5 mm d⁻¹ in July and August in 2006–2007 in central Iowa by using an instrument for recording soil moisture coupled with a heat flux calculation, whereas our estimate shows daily corn ET during July and August is 5.45 and 3.7 mm, respectively, in the same area. Chávez *et al.* [2008] reported a cornfield ET rate of 3.5 mm d⁻¹ in June and 6.5 mm d⁻¹ in July among different sites near Ames, Iowa, in 2002 by using a remote sensing method. Doraiswamy *et al.* [2001] also applied the remote sensing method to estimate ET and found corn ET ranging from 2 to 5.2 mm d⁻¹ on average across Iowa from June to August in 1990. A surface energy balance algorithm for land (SEBAL) [Bastiaanssen *et al.*, 1998a, 1998b; Allen *et al.*, 2011] has been developed to quantify ET by using satellite data. On the basis of the SEBAL heat flux data reported by Long and Singh [2012] near Ames, Iowa, and using the method introduced by Allen *et al.* [2011] to convert heat flux to ET, we estimate ET to be 3.56 mm d⁻¹. Figure 4 presents a comparison of the corn ET measurements from the literature with the estimates generated from this study in two counties in Iowa: Jasper County and Story County (where Ames is located), from which the above measurements were obtained.

[24] In addition to the previous snapshot-oriented comparison, validation of the ET simulation was conducted for all the counties within the study boundary by using a second satellite-imagery-derived ET database. Monthly data calculated by using satellite images via a heat-flux algorithm and validated by ground measurements from 1983 to 2005 by Numerical Terradynamic Simulation Group (NTSG) of University of Montana (<http://www.ntsg.umt.edu/data>) are made available to estimate ET across the U.S. continent [Zhang *et al.*, 2010]. Although the base years between the NTSG data set and our study are varied (1983–2005 versus 1970–2000), the overlapped years are long enough to offset the rare extreme climate incidents and can represent normal weather conditions. Crop layer data (USDA, <http://nassgeo-data.gmu.edu/CropScape/>) are employed to extract monthly ET values from the NTSG database only over cornfields. As seen in Figures 4 and 5, estimates of corn ET determined from this study agree extremely well with data from satellite-based estimates across more than 90 counties, while data for May, June, and September vary to some degree. ET values derived from the Penman-Monteith model appear to have wide variation from May to September, spanning from 10 to 180 mm m⁻¹, whereas values from the NTSG database have a narrower band, varying from 60 to 130 mm m⁻¹. Despite the monthly temporal variation, the sum of growing season ET values from both data sets converges eventually, leading to seasonal differences of 7%. Given the validation results, the estimates of ET values from this study appear to provide

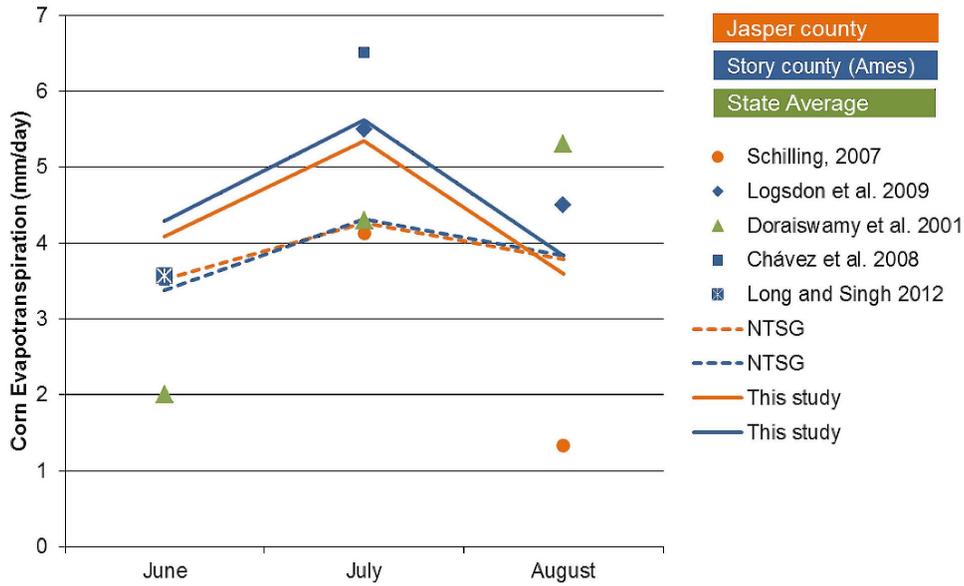


Figure 4. Comparison of monthly evapotranspiration for corn during June to August in selected counties in Iowa between the measured ET from the literature and this work. Color code represents the county location.

a reasonable blue and green water assessment for the study area. Further modeling effort would be needed to improve monthly ET modeling.

3.2. Water Footprint of Stover Ethanol

[25] Water footprints for Iowa-grown stover-based ethanol reveal substantial spatial variability, both in intensity and distribution of water type (blue, green, grey) at the county level (Figure 6). Variability of water footprint in the county level

is primarily caused by climate because rainfall volumes, frequencies, and duration are not same among the counties studied, on the basis of meteorological measurements (e.g., rain fall, humidity, wind) reported by NOAA. Even if the same crop is grown in similar soil, climate differences will lead to different green water. The variation in blue water is related to irrigation because there are still a few counties irrigated (Table S3 and Figure 7) but not related to refinery as refinery water use is process dependent, regardless of location.

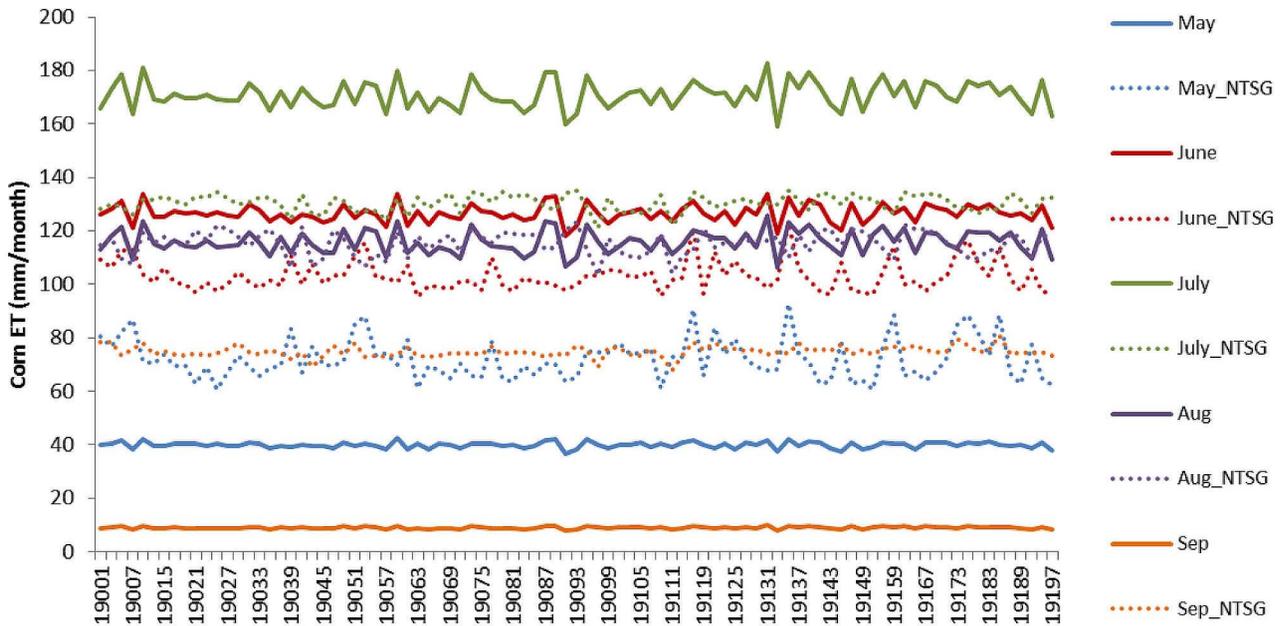


Figure 5. Temporal distribution of ET of satellite-based estimate from Numerical Terradynamic Simulation Group (NTSG) of University of Montana and that estimated in our study using Penman–Monteith equation for corn in various counties in Iowa in growing season. The numbers in x-axis represent county FIPS (Federal Information Processing Standards, <http://www.itl.nist.gov/fipspubs/geninfo.htm>). Solid line represents value from this study and dotted line indicates value from NTSG.

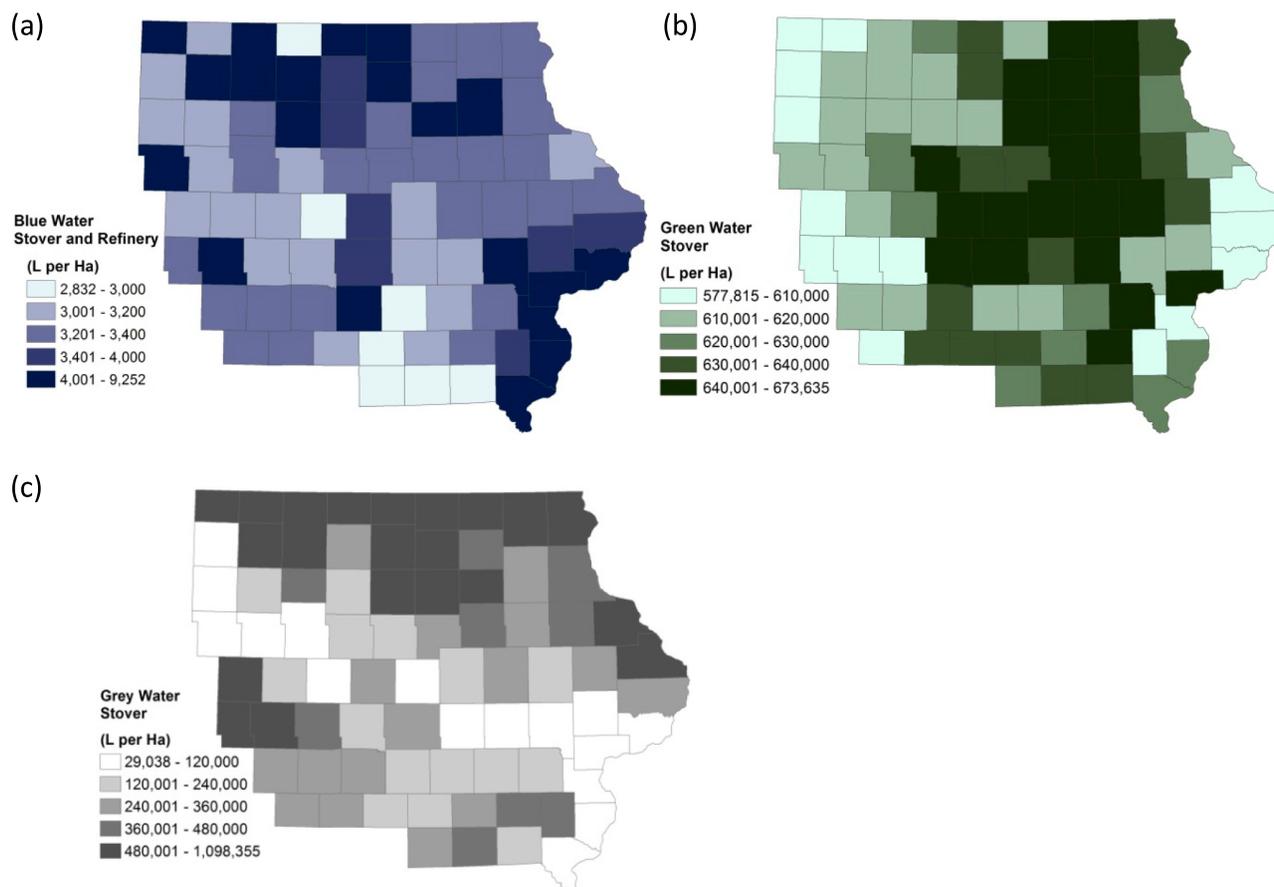


Figure 6. County-level distributions of (a) blue, (b) green, and (c) grey water footprints for corn-stover-based biofuel in Iowa; counties with zero value indicate that no corn stover is harvested for biofuel.

The spatial distribution of grey water is a result of many factors. The first factor is nitrogen loading, which varies with the crop yield, crop rotation, and fertilizer application rates (i.e., soybean does not need N fertilizer while corn does); climate (more rain fall could increase runoffs); the land topography (slope); and placement of drainage tile. These factors change from county to county. The second factor would be the natural background of nitrate (C_{NO_3}), which was determined by the USGS in the 1960s (see Table S3 for C_{NO_3} values). Together, they cause the spatial variability of grey water. On a land area basis, green water dominates the water footprint of corn-stover-derived ethanol in the Iowa counties studied. Growing one hectare of stover to produce ethanol in the studied counties harvests 577,000–673,000 L of green water (an average of 625,000 L) and requires 2800–9200 L of blue water with an average of 3700 L (Figures 6a and 6b). From a biofuel production perspective, to produce one liter of stover-based ethanol, from 760 L to 1000 L of green water and 4.6 to 13.1 L of blue water would be required. Geographically, the distribution of green water and blue water in the studied area complement each other (Figure 6), which is a combined result of soil moisture content, precipitation, and temperature. Iowa requires very minimal irrigation water for corn because the region receives plenty of rainfall during the growing season. From 1970 to 2000, Iowa received 545 mm of rain per year on average, according to NOAA

(<http://www.ncdc.noaa.gov>), and only 0.6–0.8% of corn croplands require irrigation [USDA, 2003, 2008]. It has been projected that the climate in Iowa will become wetter in next 50–100 years (Santa Clara University, The World Climate Research Programme’s Coupled Model Intercomparison Project Phase 3 (CMIP3) multimodel data set, at http://gdo-dcp.ucllnl.org/downscaled_cmip3_projections/, accessed September 2011). Given the projected increased precipitation in Iowa, the cellulosic feedstock grown in the state would have a sufficient supply of green water.

[26] The grey water footprint for corn-stover-based ethanol varies considerably, ranging from 44 to 1579 L, a 35-fold difference, with a county average of 518 L to produce one liter of ethanol, which translates to 355,000 L per hectare of cropland. The spatial distribution of grey water closely resembles that of nitrogen loadings simulated by the SWAT model. Not surprisingly, spatial variation of grey water does not follow the pattern of green water or blue water (Figure 6) since it also reflects the natural background stream concentration of the targeted compound (in this case, nitrogen) in the region, which fluctuates significantly across the state [Smith *et al.*, 2003]. Statistical analysis shows that the grey water is highly associated with the fertilizer application rate (correlation coefficient = 0.96), among other factors (e.g., crop type, soil, drainage tile, cover crop). Overall, results from this study shows the heterogeneous nature of the water issue and

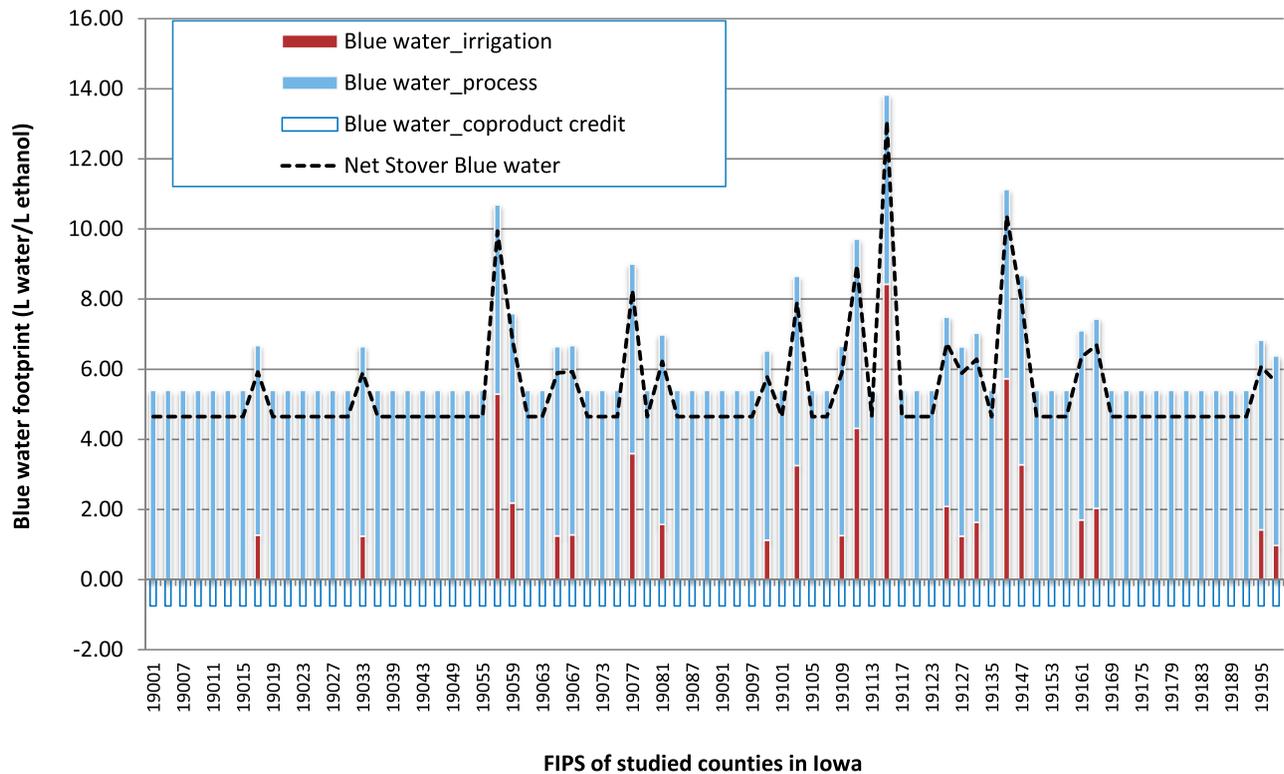


Figure 7. Blue water footprints of ethanol produced from corn stover in the studied counties in the state of Iowa. The values include irrigation water, refinery water, and coproduct blue water credit.

demonstrates the importance of increased resolution in the water footprint.

3.3. Biorefinery Blue Water Use

[27] Refinery water consumption is a key factor in determining the blue water footprint of the biofuel on a per liter fuel production basis. In fact, the blue water for stover ethanol in the studied corn-producing counties is dominated by biorefinery biochemical process water use. Of the 4.6–13.1 L of blue water, 86% is from biorefinery blue water use and only 14% is from irrigation, on average (Figure 7). As indicated in Figure 7, coproduced bioelectricity in the biorefinery plays an important role in the final water footprint accounting, providing on average 16% of the water footprint credit for the refinery blue water.

[28] A biorefinery is often built in its corresponding feedstock-producing area with an established infrastructure, to reduce costs associated with feedstock transportation. The choice of feedstock and refinery location could have significant impacts on the type and the intensity of the water footprint for cellulosic biofuel. Because a majority of water requirements in the water footprint are from the feedstock-growing stage, and a biorefinery fed by local feedstock is seen as a first choice, the magnitude of the water footprint of a particular biofuel from a refinery would be largely defined by the regional climate, soil, and feedstock yield. For example, the cellulosic ethanol produced from stover in biorefineries located in some states with similar climates and where corn yield is lower would result in a larger water footprint on a per liter of fuel basis. Therefore, it is essential to take the water resource use into consideration during refinery

site selection, to ensure proper decision making for water-sustainable production.

3.4. Limitation and Uncertainties

[29] The limitation of this approach, however, is that it requires an intensive modeling effort to develop watershed models for each region of interest. The requirements of scale and resolution would add challenges because of the maximum data set limitation in the SWAT model and the need for increased resolution for watershed and large-scale coverage. While a SWAT model for an entire country is possible, it often comes at the cost of resolution.

[30] Irrigation survey data were used to calibrate ET estimations for the crops of interest. The advantage of this method is data availability; the Crop Irrigation Survey is published by the USDA every five years. It is assumed that the data are representative of the state average. However, the survey data are highly dependent on the survey method, sample site selected, and the accuracy of individual reporting. In addition, the consumptive irrigation water use is estimated at the county level for this study, the data source of irrigation volume from the USDA irrigation survey is reported at the state level, and the irrigated acreage from the U.S. Census is available at the county level (which was not available in the irrigation survey). Thus, the irrigation water volume calibration has to be downscaled; the county estimate of irrigation volume based on irrigation acreage is calibrated by state-level data and redistributed to the county level. During data processing, additional steps would introduce statistical error.

[31] As for grey water, the data limitation lies in the N inputs value. SWAT has a crop growth model to calculate

N stress. In the “autofertilizer” modeling approach, N is added at the moment when and only when the crop needs N so that the N stress is practically zero, which is not realistic. For that reason, we adopt a field-value-based approach. Of course, this method requires a county-level fertilizer rate, which is lacking from the USDA survey. In this study, state-level data from the USDA were used as an initial input for SWAT model to generate a distributed value based on crop yield [Demissie et al., 2012].

4. Conclusions

[32] A water footprint analysis framework with increased spatial resolution can improve biofuel water sustainability assessment in evaluating complex land conversion and feedstock production scenarios. This study shows that using a watershed modeling approach in water footprint analysis significantly improves the quality of estimates of the grey water footprint by accounting for physical, chemical, and biological reactions that are associated with nutrients and their bonds to region-specific soil, landscape, land cover, and hydrodynamics. Validation of the estimated ET with measurements from plot- and field-scale data, remote sensing data, and data derived from satellite imagery revealed that the ET values modeled from this study resemble seasonal ground conditions, although the representation of monthly variation is limited. In addition, verifying ET values associated with irrigation by using irrigation survey data improves the quality and fidelity of the blue water analysis. By combining watershed modeling and water footprint life cycle analysis, the framework can be useful for conducting watershed- or county-level biofuel sustainability metric analysis to address the heterogeneity of the water footprint for various second-generation and advanced biofuel pathways.

[33] On the basis of the results, the following accomplishments have been made and conclusions drawn: (1) A spatially explicit water footprint analysis framework with improved grey water analysis for biofuel production has been introduced that incorporates SWAT watershed model into water footprint methodology to reflect hydrodynamics within a watershed. (2) Verification of the crop ET and irrigation estimate by using field data and remote sensing technology enhances the resolution of the assessment, thereby enabling an improved estimate of blue water footprint. (3) A case study demonstrated the feasibility of the framework, providing the blue, green, and grey water footprints of corn stover derived ethanol with spatial resolution at the county level.

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References

Allen, R., A. Irmak, R. Trezza, J. M. H. Hendrickx, W. Bastiaanssen, and J. Kjaersgaard (2011), Satellite-based ET estimation in agriculture using SEBAL and METRIC, *Hydrol. Processes*, 25(26), 4011–4027, doi:10.1002/hyp.8408.

Allen, R. G., L. S. Pereira, D. Raes, and M. Smith (1998), Crop evapotranspiration: Guidelines for computing crop water requirements, *FAO Irrig. Drain. Pap. 56*, Food and Agric. Organ., Rome. [Available at <http://www.fao.org/docrep/X0490E/x0490e08.htm>.]

Bastiaanssen, W. G. M., M. Menenti, R. A. Feddes, and A. A. M. Holtslag (1998a), A remote sensing surface energy balance algorithm for land (SEBAL): 1. Formulation, *J. Hydrol.*, 213(1–4), 198–212.

Bastiaanssen, W. G. M., H. Pelgrum, J. Wang, Y. Ma, J. F. Moreno, G. J. Roerink, and T. van der Wal (1998b), A remote sensing surface energy balance algorithm for land (SEBAL): 2. Validation, *J. Hydrol.*, 213(1–4), 213–229.

Chapagain, A. K., and A. Y. Hoekstra (2004), *Water Footprints of Nations*, *Value Water Res. Rep. Ser.*, vol. 16, UNESCO-IHE, Delft, Netherlands.

Chávez, J., C. Neale, J. Prueger, and W. Kustas (2008), Daily evapotranspiration estimates from extrapolating instantaneous airborne remote sensing ET values, *Irrig. Sci.*, 27(1), 67–81.

Chiu, Y., and M. Wu (2012), Assessing county-level water footprints of different cellulosic-biofuel feedstock pathways, *Environ. Sci. Technol.*, 46, 9155–9162.

Chiu, Y., B. Walseth, and S. Suh (2009), Water embodied in bioethanol in the United States, *Environ. Sci. Technol.* 43(8), 2688–2692.

Demissie, Y., E. Yan, M. Wu, and Z. Zhang (2012), Developing a watershed model for evaluation of biofuel feedstock production in the Upper Mississippi River basin, *Tech. Rep. ANL/EVS/AGEM/TR-12-07*, Argonne Natl. Lab., Argonne, Ill.

Doraiswamy, P., J. Hatfield, and J. Prueger (2001), Evapotranspiration estimates obtained from remote sensing data, *IAHS Publ.*, 267, 306–310.

Evans, J. M., and M. J. Cohen (2009), Regional water resource implications of bioethanol production in the southeastern United States, *Global Change Biol.*, 15(9), 2261–2273, doi:10.1111/j.1365-2486.2009.01868.x.

Georgescu, M., D. B. Lobell, and C. B. Field (2011), Direct climate effects of perennial bioenergy crops in the United States, *Proc. Natl. Acad. Sci. U. S. A.*, 108(11), 4307–4312, doi:10.1073/pnas.1008779108.

Gerbens-Leenes, P. W., and A. Y. Hoekstra (2009), The water footprint of sweeteners and bio-ethanol from sugar cane, sugar beet, and maize, *Res. Rep. Ser. 38*, UNESCO-IHE Inst. of Water Educ., Delft, Netherlands.

Gerbens-Leenes, P. W., A. Y. Hoekstra, and T. H. van der Meer (2009), The water footprint of bioenergy, *Proc. Natl. Acad. Sci. U. S. A.*, 106(25), 10,219–10,223.

Hoekstra, A. Y., A. K. Chapagain, M. M. Aldaya, and M. M. Mekonnen (2011), *The Water Footprint Assessment Manual: Setting the Global Standard*, Earthscan, London.

Humbird, D., R. Davis, L. Tao, C. Kinchin, D. Hsu, and A. Aden (2011), Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol, *Rep. NREL/TP-5100-47664*, Natl. Renewable Energy Lab., Golden, Colo.

Keeney, D. (2007), Will water supply limit ethanol growth in the U.S.?, paper presented at Colloquium on Water Implications of Biofuel Production in the U.S., Natl. Acad. of Sci., Washington, D. C.

Keeney, D., and M. Muller (2006), Water use by ethanol plants: Potential challenges, report, Inst. for Agric. and Trade Policy, Minneapolis, Minn.

Kent, K. M. (1972), National Engineering Handbook, sect. 4, *Hydrology*, *NEH Not. 4-102*, U.S. Dep. of Agric., Washington, D. C.

King, C. W., and M. E. Webber (2008), Water intensity of transportation, *Environ. Sci. Technol.*, 42(21), 7866–7872.

Kiniry, J. R., C. R. Tischler, and G. A. Van Esbroeck (1999), Radiation use efficiency and leaf CO₂ exchange for diverse C4 grasses, *Biomass Bioenergy*, 17(2), 95–112.

Logsdon, S. D., G. Hernandez-Ramirez, J. L. Hatfield, T. J. Sauer, J. H. Prueger, and K. E. Schilling (2009), Soil water and shallow groundwater relations in an agricultural hillslope, *Soil Sci. Soc. Am. J.*, 73(5), 1461–1468.

Long, D., and V. P. Singh (2012), A modified surface energy balance algorithm for land (M-SEBAL) based on a trapezoidal framework, *Water Resour. Res.*, 48, W02528, doi:10.1029/2011WR010607.

Marek, T., P. Colaizzi, T. A. Howell, D. Dusek, and D. Porter (2006), Estimating seasonal crop ET using calendar and heat unit based crop coefficients in the Texas High Plains evapotranspiration network, paper presented at 2006 ASAE Annual Meeting, Am. Soc. of Agric. and Biol. Eng., Portland, Oreg.

Mishra, G. S., and S. Yeh (2011), Life cycle water consumption and withdrawal requirements of ethanol from corn grain and residues, *Environ. Sci. Technol.*, 45(10), 4563–4569.

Natural Resources Conservation Service (NRCS) (1997), Irrigation guide, report, U.S. Dep. of Agric., Fort Worth, Tex.

- Neitsch, S., J. Arnold, J. Kiniry, R. Srinivasan, and J. Williams (2002), Soil and Water Assessment Tool user's manual, version 2000, *GSWRL Rep. 02-02*, Grassland, Soil and Water Res. Lab., Temple, Tex.
- Phong, V., V. Le, P. Kumar, and D. T. Drewry (2011), Implications for the hydrologic cycle under climate change due to the expansion of bioenergy crops in the midwestern United States, *Proc. Natl. Acad. Sci. U. S. A.*, *108*(37), 15,085–15,090, doi:10.1073/pnas.1107177108.
- Pradhan, A., D. S. Shrestha, A. McAloon, W. Yee, M. Haas, and J. A. Duffield (2011), Energy life-cycle assessment of soybean biodiesel revisited, *Trans. ASABE*, *54*(3), 1031–1039.
- Romaguera, M., A. Y. Hoekstra, Z. Su, M. S. Krol, and M. S. Salama (2010), potential of using remote sensing techniques for global assessment of water footprint of crops, *Remote Sens.*, *2*, 1177–1196, doi:10.3390/rs2041177.
- Schilling, K. E. (2007), Water table fluctuations under three riparian land covers, Iowa (USA), *Hydrol. Processes*, *21*(18), 2415–2424.
- Scown, C. D., A. Horvath, and T. E. McKone (2011), Water footprint of U.S. transportation fuels, *Environ. Sci. Technol.* *45*(7), 2541–2553.
- Smith, R. A., R. B. Alexander, and G. E. Schwarz (2003), Natural background concentrations of nutrients in streams and rivers of the conterminous United States, *Environ. Sci. Technol.* *37*(14), 3039–3047.
- U.S. Department of Agriculture (USDA) (2003), 2003 Farm and ranch irrigation survey, report, Washington, D. C. [Available at <http://www.agcensus.usda.gov/Publications/2002/FRIS/>.]
- U.S. Department of Agriculture (USDA) (2008), 2008 Farm and ranch irrigation survey, report, Washington, D. C. [Available at http://www.agcensus.usda.gov/Publications/2007/Online_Highlights/Fact_Sheets/Practices/fris.pdf.]
- U.S. Department of Energy (2011), U.S. billion-ton update: Biomass supply for a bioenergy and bioproducts industry, report, Washington, D. C. [Available at http://www1.eere.energy.gov/biomass/pdfs/billion_ton_update.pdf.]
- Wang, M., H. Huo, and S. Arora (2011), Methods of dealing with co-products of biofuels in life-cycle analysis and consequent results within the U.S. context, *Energy Policy*, *39*(10), 5726–5736.
- White, P. J., and L. A. Johnson (Eds.) (2003), *Corn Chemistry and Technology*, 2nd ed., Am. Assoc. of Cereal Chem., St. Paul, Minn.
- Wigmosta, M. S., A. M. Coleman, R. J. Skaggs, M. H. Huesemann, and L. J. Lane (2011), National microalgae biofuel production potential and resource demand, *Water Resour. Res.*, *47*, W00H04, doi:10.1029/2010WR009966.
- Wu, M., and M. J. Peng (2011), Developing a tool to estimate water withdrawal and consumption in electricity generation in the United States, *Rep. ANL/ESD/11-2-update*, Argonne Natl. Lab., Argonne, Ill.
- Wu, M., M. Mintz, M. Wang, and S. Arora (2009), Water consumption in the production of ethanol and petroleum gasoline, *Environ. Manage.*, *44*(5), 981–997.
- Wu, M., M. Mintz, M. Wang, S. Arora, and Y. Chiu (2011), Consumptive water use in the production of ethanol and petroleum gasoline – 2011 update, *Rep. ANL/ESD/09-1-update*, Argonne Natl. Lab., Argonne, Ill.
- Wu, M., Y. Demissie, and E. Yan (2012), Simulated impact of future biofuel production on water quality and water cycle dynamics in the Upper Mississippi River Basin, *Biomass Bioenergy*, *41*, 44–56.
- Zhang, K., J. S. Kimball, R. R. Nemani, and S. W. Running (2010), A continuous satellite-derived global record of land surface evapotranspiration from 1983 to 2006. *Water Resour. Res.*, *46*, W09522, doi:10.1029/2009WR008800.