Supporting Information

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

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1. Blue and green water

The procedure for calculating blue and green water on a county-by-county basis with national coverage follows that described in the study of Wu et al. (*1*). In this study, biofuel blue water is defined as the consumptive water contributed by irrigation—including evapotranspiration (ET) and irrigation practice losses—through the crop growth stage, as well as the process water consumed during the refinery conversion phases. By definition, green water represents the ET loss made up by precipitation. The partition between crop blue water and green water relies on the estimation of local effective rain and total ET during the crop-growing seasons. Thus, theoretically, the crop total water demand should be satisfied by effective rain and irrigation together, and is calculated on a monthly basis in this study. However, owing to the natural variances in crop tolerance to droughts, irrigation practices may not necessarily make up the entire net ET loss after the occurrence of effective rain. Therefore, the calculated irrigation volume must be calibrated and validated with actual irrigation reports in order to achieve a better estimate. As suggested in the study of Wu et al. (*1*), the Farm and Ranch Irrigation Survey (*2-4*) can be employed for irrigation water justification.

To allocate blue and green water among corn grain and stover, or wheat grain and wheat straw, we assume the water burden should be shared proportionally by the grain and residue used for generating ethanol on the mass basis. If residue is not used for ethanol production, it remains as agricultural waste and is not responsible for water consumption (see section 3 in this document).

2. Grey water

Grey water volume is defined as the virtual water quantity required to assimilate the pollutant load from the permissible standards down to the natural background concentration, and is calculated by the following equation (*5*):

$$GyW = \frac{L_{NO_3}}{NO_{3\,permit} - C_{NO_3}} \qquad \text{(S1)}$$

where

GyW is nitrate grey water, in m^3,

L_{NO3} is the nitrate loading (kg/yr) in local streams as a result of nitrogen fertilizer leaching,

$NO_{3\,permit}$ is the permissible nitrate concentration in stream water set by the EPA, i.e., 0.01 $kg/m^3/yr$, and

C_{NO3} is the natural-background total nitrate concentration ($kg/m^3/yr$), which can be derived from Smith et al. (*6*).

To estimate the nitrate loading (L_{NO3}) in water bodies, we designate a factor of the fraction nitrogen leached (kg/yr) into the streams (output) in total nitrogen fertilizer applied (kg/yr) in the fields (input) noted as NOI on a county basis by different feedstock:

$$L_{NO3} = N_i \times NOI_i \times 0.95 \qquad \text{(S2)}$$

where N_i is the nitrogen application (kg N/yr) in a county for feedstock i which is converted to nitrate by a factor of 0.95 indicating the fraction of nitrate in total nitrogen. The state-level application data (kg N per unit area) are available in the ERS/USDA report (*7*), and we assume all the counties in a state share the same fertilizer input amount per area, except for corn and soybean grown in the Upper Mississippi River Basins (UMRB). If a county is located within the UMRB region, we employed the fertilizer application simulated by Wu et al. (*8*), in which the fertilizer application is determined by crop nutrient demand using a SWAT model. For counties out of the UMRB boundary, we use the available state-level fertilizer application rates from ERS/USDA (*7*).

As for NOI_i, two alternative approaches are adopted, again, depending on the location of a county (Figure S1). If a county is situated within UMRB, the SWAT modeled output of NOI values are derived from the work of Wu et al. (*8*). Otherwise, data from the USGS (*9-15*) computed using SPARROW are applied.

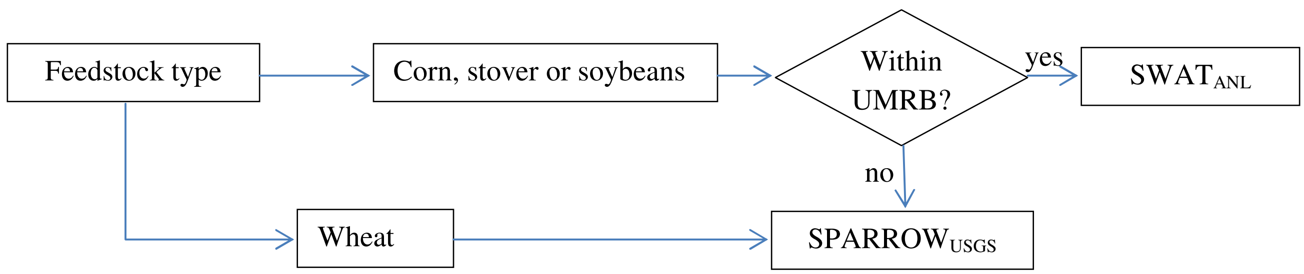

Fig. S1 Diagram of model selection to determine NOI values. To estimate NOI for corn, corn stover, and soybeans grown in counties located in the Upper Mississippi River Basin (UMRB), the SWAT-based values estimated by Argonne National Laboratory (SWAT$_{ANL}$) are applied; for other NOIs, the SPARROW-based values calculated by the USGS (SPARROW$_{USGS}$) are applied.

The SPARROW model established by the USGS has made the relationships between nitrogen inputs and loading among corn-soybean mixed fields and wheat growing areas separately available based on the 1992 agricultural data. The relationships between nitrogen inputs and loading are only available for agricultural lands without distinguish crop types if using 2002 as a base year. However, we find that the crop-specific data based on 1992 agricultural information indicate a strong correlation between agricultural-land NOI in 1992 and that of corn/soybean and wheat fields during the same year (*9*). Therefore, we derive the correlations and apply the 2002 agricultural-land NOI to estimate corn/soybean (NOI$_{corn\text{-}soy}$) and wheat-field NOIs (NOI$_{wheat}$) as Table S1. Notably, neither model covers the southwestern states in 2002, including California, Nevada, Utah, Arizona, Colorado, and New Mexico. For counties of these states, we assume the local NOI values associated with corn and soybeans in 2002 remain the same as that in 1992. For soybean fields, we assume the nitrogen input and loading ratio is the same as for corn-soybean mixed land. The selections of equations are summarized in Table S2.

Table S1. Equations for converting ratios of nitrogen input and loading from 1992 to 2002. NOI_{cs}, NOI_{wht}, and NOI_{ag} denote nitrogen input and loading ratio of corn-soybean mixed lands, wheat, and total agricultural areas. In some rare circumstances, the nitrogen input and loading ratios from corn-soy mixed lands and wheat fields in 1992 ($NOI□_{cs}$, and $NOI□_{wht}$) are treated as a constant input factor to improve the regression fitness of each other's counterpart.

HUC2	$NOI_{cs}= f\,(NOI_{ag})$	R^2	$NOI_{wht}= f\,(NOI_{ag})$	R^2
1, 2	$\ln(NOI_{cs}) = 0.986 \ln(NOI□_{wht}) +0.041 \ln(NOI_{ag}) +0.246$	0.96	$\ln(NOI_{wht}) = 0.9471\ln(NOI□_{cs}) +0.003 \ln(NOI_{ag}) -0.270$	0.96
3	$NOI_{cs} = 0.702NOI_{ag}^{0.657}$	0.77	$NOI_{cs} = 0.677NOI_{ag}^{0.731}$	0.70
4 – 6	$NOI_{cs} = 0.039\ NOI_{ag} +1.093\ NOI□_{wht}+0.014$	0.92	$NOI_{wht} = 0.055\ NOI_{ag} +0.772\ NOI□_{cs} +0.004$	0.92
7, 8	$NOI_{cs} = 0.098\ NOI_{ag} +1.092\ NOI□_{wht} +0.003$	0.97	$NOI_{wht} = -0.0368\ NOI_{ag} +0.864\ NOI_{cs} -0.0002$	0.53
9, 10	$\ln(NOI_{cs}) = 0.814 \ln(NOI_{ag}) -0.059$	0.79	$\ln(NOI_{wht}) = 0.835 \ln(NOI_{ag}) -0.190$	0.86
11, 12	$\ln(NOI_{cs}) = 1.054 \ln(NOI_{ag}) +0.726$	0.92	$\ln(NOI_{wht}) = 1.002 \ln(NOI_{ag}) +0.385$	0.93
13 – 16	$\ln(NOI_{cs}) = 1.008 \ln(NOI_{ag}) +0.650$	0.95	$\ln(NOI_{wht}) = 1.001 \ln(NOI_{ag}) +0.426$	0.92
17, 18	$\ln(NOI_{cs}) = 0.9656 \ln(NOI_{ag}) +0.575$	0.94	$\ln(NOI_{wht}) = 0.962 \ln(NOI_{ag}) +0.367$	0.94

Table S2. Nitrogen input and loading (NOI) assumptions and model selections in this study.

Feedstock	Location	NOI data sources
Corn grain	In UMRB	Wu et al. (2012), Scenario: corn-soy mixed
	Out of UMRB	USGS (2002) and equations in Table S1
Corn stover	In UMRB	Wu et al. (2012), Scenario: corn-soy mixed
	Out of UMRB	USGS (2002) and equations in Table S1
Soybean	In UMRB	Wu et al. (2012), Scenario: corn-soy mixed
	Out of UMRB	USGS (2002) and equations in Table S1
Wheat straw	In UMRB	USGS (2002) and equations in Table S1
	Out of UMRB	USGS (2002) and equations in Table S1

Grey-water volume associated with stover accounts for corn-growing grey water allocated to stover plus that resulting from supplemental fertilizer application to make up nutrient loss caused by stover removal. The supplemental fertilizer requirement (N_s, kg N/yr) is assumed to be a fixed value of 7.22 kgN per hector of corn harvested area (*8*). For the rest of the feedstock types, grey-water volume is directly allocated following the same fashion as applied in the blue and green water (see next section). The choice of baseline year can affect nitrogen loading values owing to the climate variations. The effects can be significant when the extreme weather condition occurs in a given year at a particular region. For the grey water, data years are from 2002 to 2006, during which no extremely wet or dry year has been recorded in the U.S.

3. Water allocation

Blue, green and grey water volumes for each type of crop are allocated into crop grain and its residue collected for ethanol production based on the crop harvest index (HI) and residue removal assumption.

- Corn grain and stover

  Corn HI = 0.5 (*16*), and stover removal fraction = 24%

  Blue and Green water allocated to corn grain = 0.5/(0.5+0.5×24%) = 0.806

  Blue and Green water allocated to corn stover collected for ethanol production = 1−0.806 = 0.194

  Grey water resulted from fertilizer application at the initial stage is allocated to corn grain and stover following the same fractions as blue and green water. Grey water resulted from supplemental fertilizer application for recovering nutrient loss associated with removing stover is 100% allocated to stover.

- Soybean

  No residue collected for biofuel, thus 100% of water allocated to soybean.

- Water associated with wheat and wheat straw

  Wheat HI = 0.38 (*17*), and wheat straw removal fraction = 30%

  Water allocated to wheat straw collected for ethanol production = (1−0.38)×30%/((1−0.38)×30%+0.38) = 0.329

  All blue, green and grey water is allocated using the same partition.=

4. Coproduct credits

Historically, five methods have been applied for energy allocation in life cycle analysis based on: (1) mass, (2) product energy content, (3) system expansion or displacement, (4) process energy, and (5) market value of the products. A previous study found that different allocation methods may not necessarily lead to distinctive results under different impact categories, especially water-related impact indicators (*18*). The magnitude of effects caused by allocation method selection may vary depends on the nature of the studied product and the distinctness between the studied product and its coproducts (*19*), which is beyond the scope of this study.

We compared these five methods for the purpose of water footprint. Methods based on energy content of the product (2) and process energy (4) would not be suitable because energy content of a product may not be linearly related to the water content, especially when it is fuel. Market based method

(5) is reasonable, however, there is no commercial data available for the study to begin with given that the cellulosic feedstock market has yet to be established in the U.S. System expansion (3) is usually preferred in LCA representing the resultant input/burden savings by displacing another product, which is found suitable for our study. The refinery net water use assumptions after factoring in coproduct credits are listed in Table S3.

Table S3. Refinery process water consumption on the per-liter biofuel production basis.

Pathway	Feedstock	Conversion Process	Blue Water	Unit	Reference
Corn-to-ethanol	Corn grain	Fermentation, dry milling	2.72	L water/L biofuel	Argonne National Lab (*20*)
Corn stover-to-ethanol	Corn stover	Biochemical	5.40	L water/L biofuel	Humbird et al. (*21*)
Soybean-to-biodiesel	Soybean	Physical/chemical	0.77	L water/L biofuel	Argonne National Lab (*20*)
Wheat straw-to-ethanol	Wheat straw	Biochemical	5.40	L water/L biofuel	Humbird et al. (*21*)

We find that each kilogram of corn for fuel can displace 0.25 kg of corn, and 0.14 kg of soybean which is attributed to the production of distillers grains with solubles (DDGS) in the corn-ethanol dry milling (*20*). Thus, the irrigation consumption associated with this portion of DDGS can be treated as water credit of corn ethanol. Each liter of corn ethanol can also displace 0.017 liters of blue water consumption in producing urea (*22*) displaced by DDGS. Water credits embodied in displacing DDGS irrigation and urea production should be deducted from corn ethanol blue water footprint. The glycerin produced in the soybean biodiesel processing can displace epichlorohydrin glycerin, with which 0.65 liter of groundwater can be credited back to soybean biodiesel blue water footprint (*22*).

For the cellulosic feedstocks of corn stover and wheat straw, bioelectricity is generated as a coproduct during the biochemical conversion process. It is estimated that 0.476 kWh of bioelectricity is produced per liter of ethanol produced (*21*). Incorporating water consumption associated with the electricity generation using a power water tool (*20*), the blue-water savings resulting from displacing conventional U.S. electricity mix with bioelectricity translates to a coproduct credit of 248.68 liters water per dry metric ton of cellulosic feedstock.

The grey-water volumes for stover and wheat straw are not affected by the coproduct credits, as the study only focuses on nutrient-associated grey water and the electricity generation does not yield substantial grey water containing nitrogen or phosphorus.

5. Sensitivity analysis results

The sensitivity analysis results indicate that blue, green and grey water is sensitive to the change of ethanol yield assumptions, in which green water is also sensitive to the estimates of climate factors. Grey water estimates are significantly affected by the assumptions of nitrogen input and loading ratios (Fig. S2). By comparing the results derived from SWAT and SPARROW models using the Upper Mississippi River Basin corn simulation as an example, these two models agree with each other very well on the input data of fertilizer application (Fig. S3). However, the fraction of nitrogen loading in total fertilizer input is less sensitive to the characteristics of each watershed in SPARROW (Fig. S4). As a result, SPARROW falls short to capture the extreme cases and delivers a more homogeneous distribution of nitrogen input and loading pattern than SWAT (Fig. S5). Therefore, the estimation of grey water still requires detailed local analysis in order to improve the numerical quality.

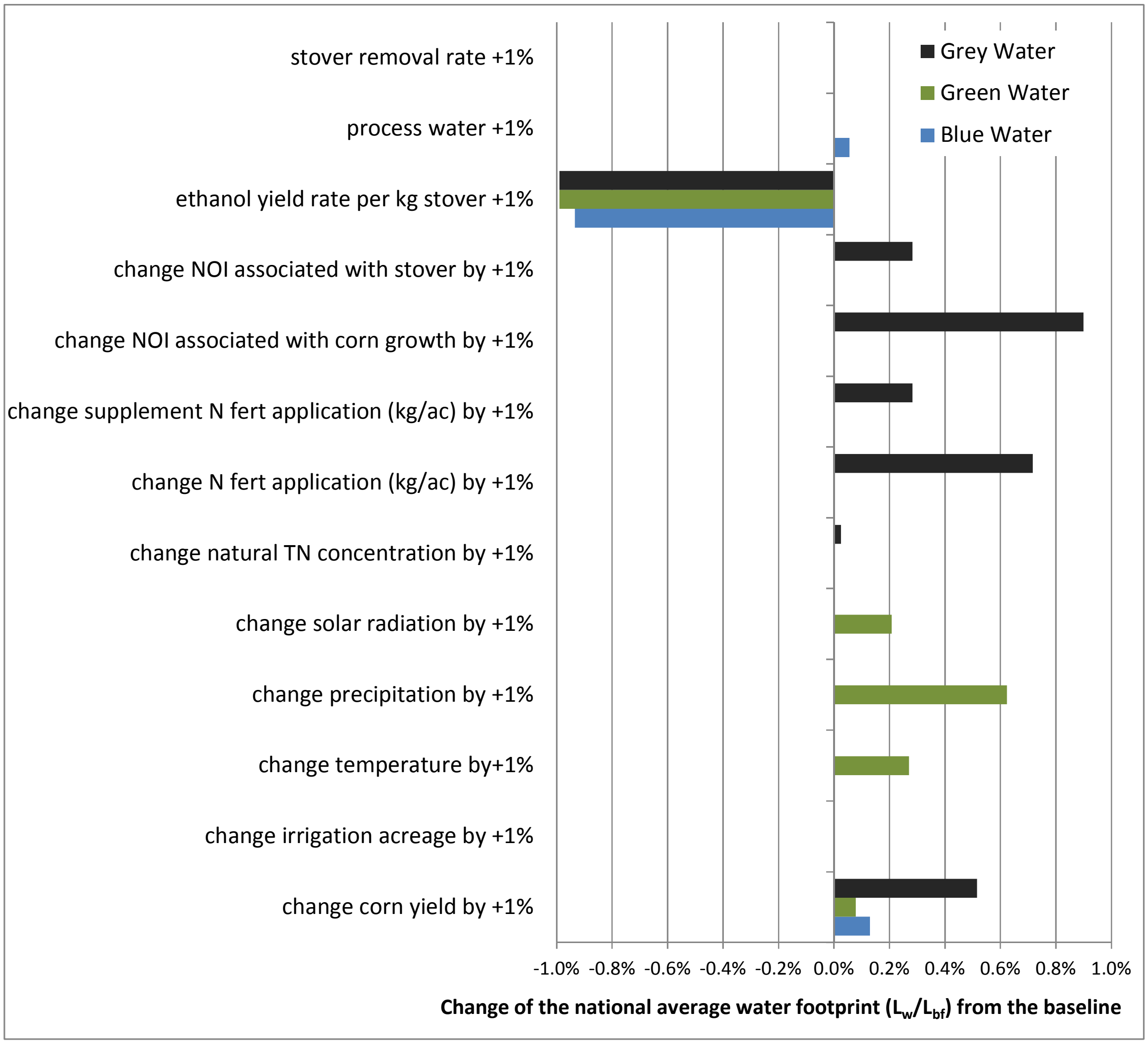

Fig. S2. Sensitivity test of the national averaged blue, green and grey water embodied in corn stover ethanol under the perturbation of each factor by 1%.

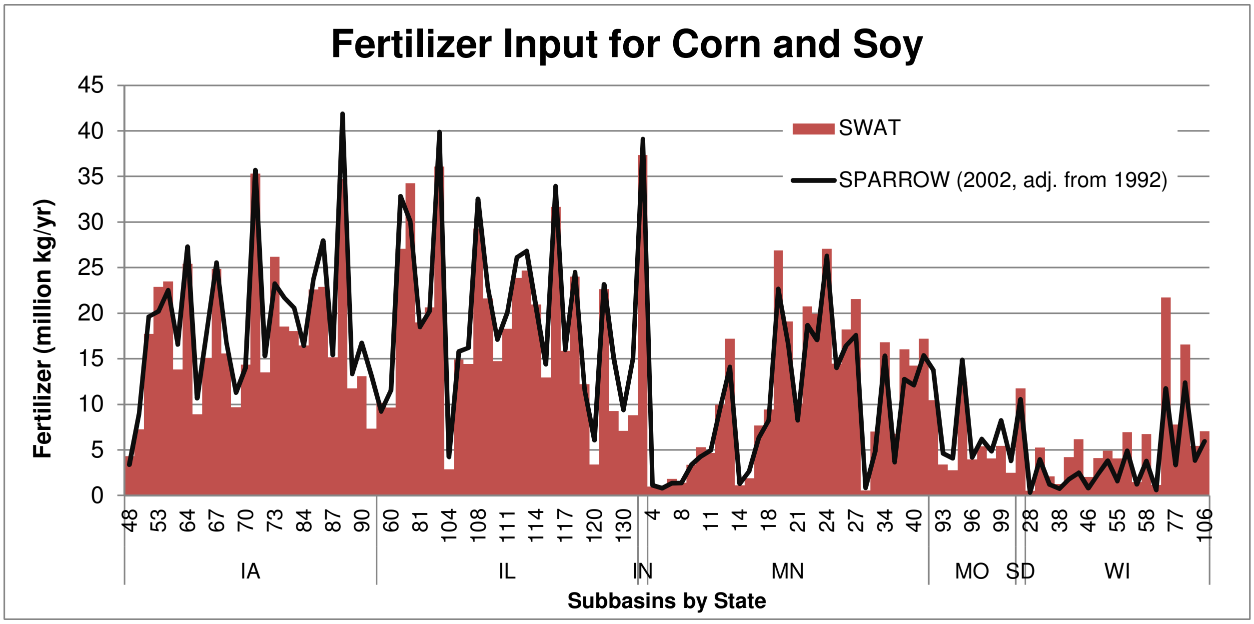

Fig. S3. Fertilizer application as an input data for SWAT and SPARROW fits well in the two models within the Upper Mississippi River Basin.

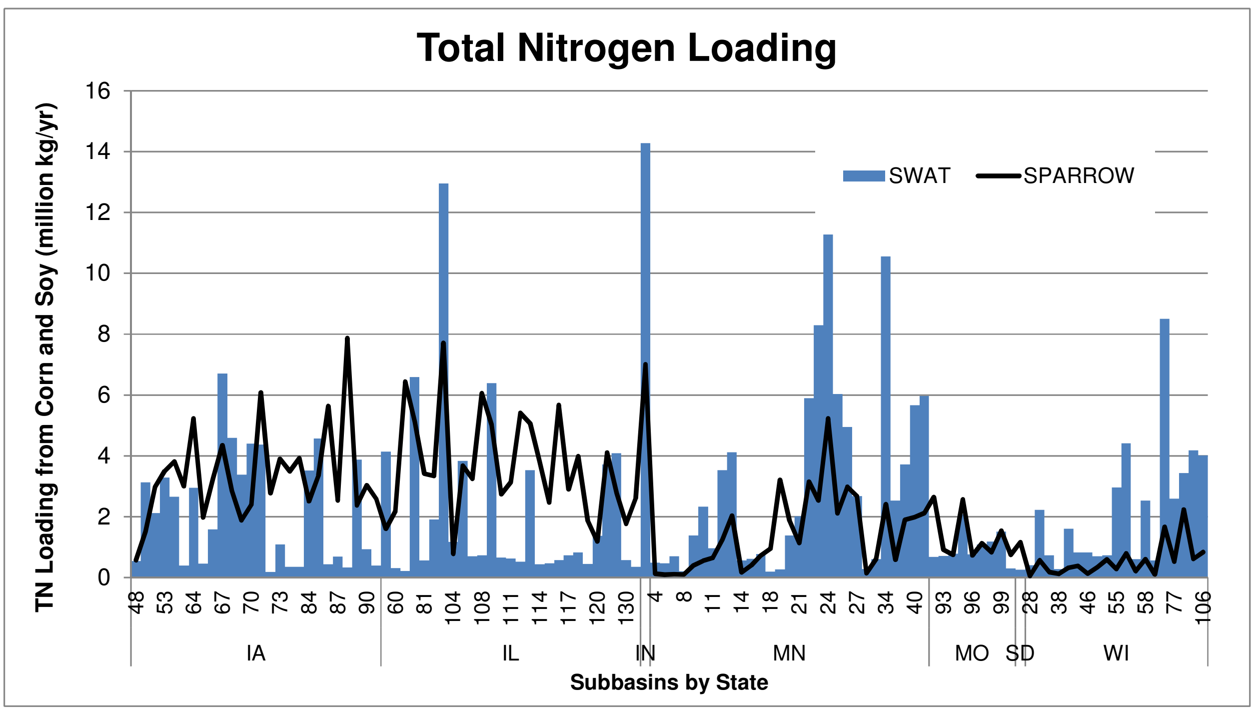

Fig. S4. SPARROW appears to have the tendency to overestimate nitrogen loading in Iowa and Illinois, whereas it tends to underestimate that at Minnesota and Wisconsin.

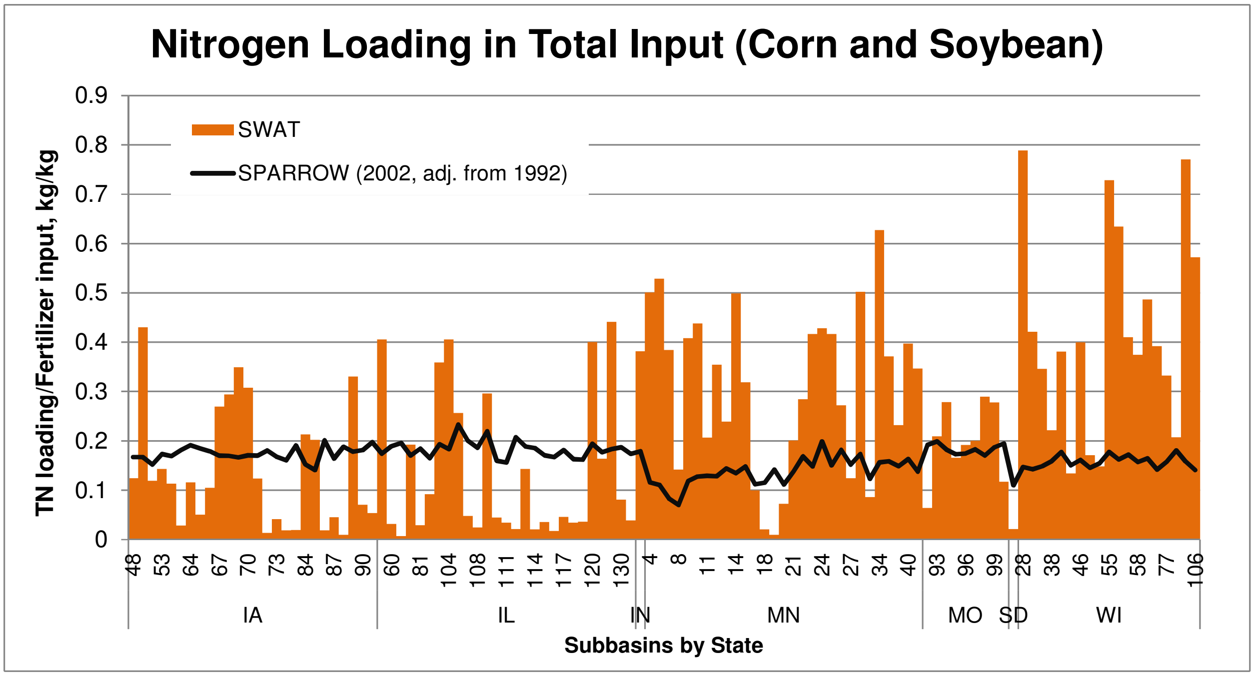

Fig. S5. SPARROW shows a more homogeneous ration between nitrogen loading and fertilizer input than SWAT.

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