## **Supporting Information**

## Gerbens-Leenes et al. 10.1073/pnas.0812619106

## SI Methods

Calculation of the Water Footprint (WF) of Crops. For the calculation of the WF of crops, this study used the methodology of the WF concept (1). There is an extensive database that includes the WF of almost all crops produced worldwide (m³/ton), based on average national meteorological data (2). This study, however, assessed the WFs of crops more specifically by production location. WF calculations were made by adding up daily crop evapotranspiration (mm/day) over growing periods, thus providing information on crop water requirements. The start of the growing season depends on climatic conditions in the production location and on the individual choices of farmers. For the start of the growing season, this study took the first option for sowing after winter or after a dry season, assuming that growing seasons start when mean monthly maximum temperatures are above 10 °C and when sufficient rain and global radiation is available.

This study calculated crop water requirements in the main producing countries for the 12 crops shown in Table S1 and for jatropha, distinguishing between the green and the blue WF, but excluding the gray WF. Next, the main producing countries, deriving data from the Food and Agriculture Organization (FAO), were selected (3). For jatropha, it considered production in Brazil, Guatemala, Indonesia, and Nicaragua, countries whose data were available (4). Next, agricultural production locations were selected. Information was obtained from the Madison Center for Sustainability and the Global Environment of the University of Wisconsin (5). For these areas, weather stations providing climatic data, that were used as input for the calculations, were selected. Data were drawn from Müller and Hennings (6).

The calculation of crop water requirements (mm/day) was performed by major production region, by using the calculation model CROPWAT 4.3 (7) based on the FAO Penman–Monteith method, to estimate reference crop evapotranspiration (8) and a crop coefficient that corrects for the difference between actual and reference crops.

Calculations for green and blue WFs (m<sup>3</sup>/ton) were performed by using Hoekstra and Chapagain's method (1). Green water use (m<sup>3</sup>/ha) over the length of the growing period was calculated as the sum of daily volumes of rainwater evapotranspiration. This green water use is equal to the crop water requirement except when effective precipitation is less than the requirement, in which case rainwater evapotranspiration is equal to effective precipitation. Blue water use (m<sup>3</sup>/ha) over the length of the growing period was calculated as the sum of daily volumes of irrigation-water evapotranspiration. This blue water use is equal to the irrigation requirement, if this requirement is actually met, and otherwise to actual effective irrigation. The irrigation requirement is defined as the crop water requirement minus effective precipitation. In doing so, it has been assumed that irrigation requirements are actually met. The green WF of a crop (m<sup>3</sup>/ton) is the total green water use over the length of the growing period (m<sup>3</sup>/ha) divided by the crop yield (ton/ha). The blue WF (m<sup>3</sup>/ton) is the total blue water use over the length of the growing period (m<sup>3</sup>/ha) divided by the crop yield (ton/ha). In general, yields show variations over the years. This study, therefore, calculated average yields over 5 production years (1997-2001) by using data from the FAO (3).

Calculation of the WF of Heat and Electricity from Biomass. The energy content of biomass is expressed in terms of combustion values. Energy analysis defines the energy content of a substance

as the amount of heat produced during combustion at 25 °C at 1 bar. It distinguishes between the higher heating value (HHV) and the lower heating value (LHV) (9). For the HHV, energy analysis measures the heat content of water that is the product of the combustion process in the liquid form; in the case of LHV, energy analysis measures the heat content of water that is the product of the combustion process in the gaseous form. For the calculation of the WF of heat from biomass, this study has followed the method of Gerbens-Leenes, et al. (10), which calculates the energy yield of a crop [gigajoule (GJ)/ton] by combining data on the heat of combustion of plant components with information on composition, harvest index, and dry-mass fraction of a crop as shown in Tables S4 and S5:

$$E_{heat}(c) = HI(c) \times DMF_{y}(c) \times \sum_{i=1}^{5} (f_{y,i} \times HHV_{i})$$

+ 
$$(1 - HI(c)) \times DMF_r(c) \times \sum_{i=1}^{5} (f_{r,i} \times HHV_i)$$

 $E_{\rm heat}(c)$  is the energy yield of crop c in the form of heat (GJ/ton), HI(c) the harvest index of crop c (g/g),  $DMF_y(c)$  the dry-mass fraction of the crop yield (g/g),  $DMF_r(c)$  the dry-mass fraction in the rest fraction (i.e., in the residue biomass),  $f_{y,i}$  the fraction of component i in the dry mass of the crop yield (g/g),  $f_{r,i}$  the fraction of component i in the dry mass of the rest fraction (g/g), and  $HHV_i$  the higher heating value of component i [kilojoule (kJ)/g].

For the generation of electricity from biomass, industry can use the heat that becomes available from the combustion of total biomass. The energy in the form of electricity from crop c (GJ/ton) depends on the efficiency with which energy in the form of biomass-heat can be transformed into electricity:

$$E_{electr}(c) = \eta \times E_{heat}(c)$$

For the value of the efficiency  $\eta$ , this study applied a value of 59%, based on the maximum efficiency derived from Carnot (11) and the technology of "Biomass fired Integrated Gasifier Combined Cycle" operated at a temperature of 720 K (9, 12).

The WF of heat from a crop c (m³/GJ) was calculated by dividing the WF of the crop (m³/ton) by the heat content of the crop (GJ/ton). The WF of biomass electricity from a crop c (m³/GJ) was calculated by dividing the WF of the crop (m³/ton) by the electricity output per crop unit (GJ/ton):

$$WF_{heat}(c) = \frac{WF(c)}{E_{heat}(c)}; \qquad WF_{electr}(c) = \frac{WF(c)}{E_{electr}(c)}$$

Calculation of the WF of First-Generation Biofuels. Currently, bioethanol is produced from sugars that come from sugar cane or sugar beet, or from starch hydrolysed into sugars derived from maize, wheat, or cassava (13). Under anaerobic conditions, sugar naturally ferments into acids and alcohols (mainly ethanol). For thousands of years people have used yeast to hasten fermentation. The main metabolic pathway involved in ethanol fermentation is glycolysis, through which 1 molecule of glucose is metabolized and 2 molecules of pyruvate are produced (14, 15). Under anaerobic conditions, pyruvate is further reduced to ethanol, with the release of CO<sub>2</sub>. The overall reaction is  $C_6H_{12}O_6 \rightarrow 2$   $C_2H_5OH + 2CO_2$ . Theoretically, the maximum yield of

ethanol is 511 g of ethanol and 489 g of carbon dioxide per kg of glucose metabolized (or 530 g of ethanol per kg of starch). Often, various by-products are also produced, for example, glycerol (15). During ethanol fermentation, yeast cells suffer from stresses, such as ethanol accumulation, inhibiting yeast cell growth and ethanol production. The final ethanol concentration is  $\approx 10-12\%$  (15, 16). The fermentation industry, therefore, uses a tanks-in-series system to alleviate product inhibition. Currently, it can reach a yield of 90-93% of the theoretical value of glucose to ethanol (17).

Oilseed crops, such as rapeseed, soybean, and jatropha, are used to produce either straight vegetable oil or biodiesel. Straight vegetable oil is oil extracted from an oilseed crop and directly used for energy purposes (13). An example is olive oil for lighting. Because of its chemical properties, such as the high viscosity at low temperatures, it is often difficult to use straight vegetable oil as a biofuel in diesel engines (13). In countries with warm climates, the relatively high temperatures prevent the oil from thickening and straight vegetable oil is a viable fuel. In countries with temperate climates, the oil needs additional treatment to make a biodiesel that is less sensitive to lower temperatures. Biodiesel is manufactured in a chemical reaction termed transesterification, in which oil reacts with an alcohol resulting in an alkyl ester of the fatty acid, with glycerine molecules as the primary coproduct. In Europe, rapeseed oil is the dominant feedstock for biodiesel, with some sunflower oil also used. In the U.S., the main feedstock is soybean oil, and in tropical and subtropical countries, palm, coconut, and jatropha oils are used (13).

When calculating natural resource use, the whole life cycle of a product should be taken into account. The use of water, however, is predominantly during the first link of the production chain—agriculture. Ethanol production, for example, requires ≈21 L of water per L of ethanol, but this water is often reused (18). This study, therefore, only took water requirements in agriculture into account and ignored water use in the industrial links of the production chain.

The ethanol-energy yield of a crop (in GJ/ton) was calculated as follows:

$$E_{ethanol}(c) = DMF_{y}(c)f_{carbohydr}(c)f_{ethanol} \times HHV_{ethanol}$$

where  $DMF_y(c)$  is the dry-mass fraction in the crop yield (g/g),  $f_{\rm carbohydr}(c)$  the fraction of carbohydrates in the dry mass of the crop yield (g/g),  $f_{\rm cthanol}$  the amount of ethanol obtained per unit

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of carbohydrate (g/g), and  $HHV_{ethanol}$  the higher heating value of ethanol (kJ/g). For the amount of ethanol per unit of sugar, we assumed the theoretical maximum value of 0.51 g/g, and for starch, 0.53 g/g (17).

The biodiesel-energy yield of a crop (in GJ/ton) was calculated as follows:

$$E_{diesel}(c) = DMF_{v}(c) \times f_{fat}(c) \times f_{diesel} \times HHV_{diesel}$$

where  $DMF_y(c)$  is the dry-mass fraction in the crop yield (g/g),  $f_{\rm fat}(c)$  the fraction of fats in the dry mass of the crop yield (g/g),  $f_{\rm diesel}$  the amount of biodiesel obtained per unit of fat (g/g), and  $HHV_{\rm diesel}$  the higher heating value of biodiesel (kJ/g). For the fraction biodiesel per fat weight, we assumed the value of 1. The fractions of carbohydrates and fats in the dry mass of crop yields are given in Table S5. Table S6 gives the HHVs of ethanol and biodiesel.

The WF of ethanol energy from a crop c (m³/GJ) was calculated by dividing the WF of the crop (m³/ton) by the ethanol energy yield of the crop (GJ/ton). The WF of biodiesel energy from a crop c (m³/GJ) was calculated in a similar way:

$$WF_{ethanol}(c) = \frac{WF(c)}{E_{ethanol}(c)}; \qquad WF_{diesel}(c) = \frac{WF(c)}{E_{diesel}(c)}$$

For the calculation of the WF of first-generation biofuels, this study fully allocated the WF of the crop to the biofuels derived, assuming that the value of the residues of production was much lower than the value of the biofuel.

Calculation of the WF of Next-Generation Biofuels. Biomass not only contains starch, sugar, and oil that can be processed into biofuels, it also contains large amounts of cellulosic matter. Thus far, the cellulosic fraction could be used for energy only by burning it to provide heat and produce electricity. It is expected that these cellulosic fractions will form an attractive source for the production of liquid, next-generation biofuels for which industry can use total biomass, including wastes. It is not yet clear what efficiency will be achieved in converting total biomass into biofuel. It is safe, however, to assume that the WF of next-generation biofuels will never be lower than the WF of the crop (m³/ton) divided by the energy content of the crop (GJ/ton), where the latter is expressed in terms of its HHV.

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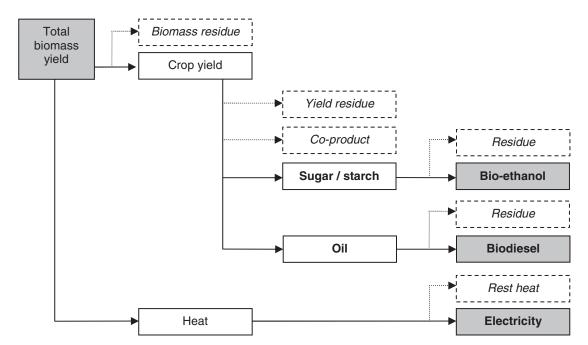


Fig. 51. From biomass to bioenergy. Total biomass yield can be converted into heat and subsequently into electricity. Alternatively, the crop yield, which is part of the total biomass, can be converted into bioethanol (in the case of starch and sugar crops) or biodiesel (in the case of oil crops). In every step in the production chain, residues or rest heat are generated.

Table S1. The 12 crops that contribute 80% of total global crop production

Crop	Average global production for 1997–2001, 10 <sup>6</sup> ton/yr
Sugar cane	1,258
Maize	603
Wheat	594
Paddy rice	593
Potato	309
Sugar beet	253
Rye	220
Cassava	172
Soybean	160
Barley	140
Sorghum	59
Rapeseed	38
Total	4,401
Total global crop production (1997)	5,513

See ref. 19.

Table S2. Overview of the extreme values of total WFs and blue WFs per crop, m³/ton

Crop	Country	Extreme values total WF, m³/ton	Country	Extreme values blue WF, m³/ton		
Barley	Ireland	448	India	147		
	Kazakhstan	6,540	Kazakhstan	6,510		
Cassava	India	191	India/Vietnam	0		
	Côte d'Ivoire	1,437	Côte d'Ivoire	1,437		
Jatropha	Brazil	3,222	Brazil	1,170		
•	India	21,729	India	14,344		
Maize	Spain	407	South Africa	0		
	Nigeria	3,783	Nigeria	2,267		
Rapeseed	Germany	1,482	Bangladesh	0		
•	India	9,900	Pakistan	4,130		
Paddy rice	Egypt	634	Bangladesh	19		
•	Nigeria	6,471	Nigeria	4,629		
Potato	Spain	85	Japan	0		
	Kazakhstan	922	Kazakhstan	922		
Rye	Sweden	637	Austria	245		
	Russia	2,620	Russia	1,220		
Sorghum	Egypt	525	Venezuela/Chad	0		
	Niger	24,700	Sudan	14,117		
Soybean	Italy	1,442	Paraguay	546		
	India	7,540	Indonesia	2,583		
Sugar beet	Morocco	56	Japan	0		
	Russia	455	Russia	376		
Sugar cane	Peru	108	Peru	8		
-	Cuba	524	Pakistan	217		
Wheat	Denmark	513	Australia	0		
	Kazakhstan	10,178	Kazakhstan	9,989		

Table S3. Energy provided by ethanol from 2 sugar and 10 starch crops that were included in this study, as well as the energy provided by oil from the 3 oil crops

Crop	Megajoule of biofuel per kg of fresh weight crop					
Ethanol from sugar						
Sugar cane	2.3					
Sugar beet	2.6					
Ethanol from starch						
Potato	3.1					
Cassava	5.2					
Sorghum	10.0					
Maize	10.0					
Wheat	10.2					
Barley	10.2					
Paddy rice	10.5					
Rye	10.5					
Biodiesel from oil						
Soybean	6.4					
Rapeseed	11.7					
Jatropha	12.8					

Table S4. HHV for 6 major groups of plant components

Plant component	HHV, kJ/g			
Carbohydrates	17.3			
Proteins	22.7			
Fats	37.7			
Lignins	29.9			
Organic acids	13.9			
Minerals (K,Ca,P,S)	0.0			

See ref. 9.

Table S5. Main characteristics for 12 crops

				Paddy						Sugar	Sugar	
	Cassava	Barley	Maize	rice	Potato	Rapeseed	Rye	Sorghum	Soybean	cane	beet	Wheat
Harvest index	0.70a	0.42a	0.45a	0.42	0.70a	0.32ª	0.42	0.42	0.40a	0.60a	0.66a	0.42a
Economic yield	tuberb	ear + grain <sup>b</sup>	whole tops <sup>b</sup>	inflor + grain	tuber <sup>b</sup>	inflor + seed <sup>d</sup>	ear + grain <sup>b</sup>	ear + grain <sup>b</sup>	beansa	whole topsa	beeta	ear + grain <sup>b</sup>
Dry mass <sup>b</sup>	0.38	0.85	0.85	0.85	0.25	0.74	0.85	0.85	0.92	0.27	0.21	0.85
Composition dry mass, g/100 g <sup>c</sup>												
Carbohydrates	87	76	75	76	78	7	76	76	29	57	82	76
Proteins	3	12	8	8	9	22	12	12	37	7	5	12
Fats	1	2	4	2	0	42	2	2	18	2	0	2
Lignins	3	6	11	12	3	2	6	6	6	22	5	6
Organic acids	3	2	1	1	5	1	2	2	5	6	4	2
Minerals (K, Ca, P, S)	3	2	1	1	5	26	2	2	5	6	4	2
Rest fraction	leaves	shells	stems	stems	leaves	leaves	stems	stems	leaves	stems	leaves	stems
Dry mass <sup>b</sup>	0.38	0.85	0.85	0.85	0.13	0.13	0.85	0.85	0.15	0.27	0.21	0.85
Composition dry mass, g/100 g <sup>c</sup>												
Carbohydrates	52	62	62	62	52	52	62	62	52	62	52	62
Proteins	25	10	10	10	25	25	10	10	25	10	25	10
Fats	5	2	2	2	5	5	2	2	5	2	5	2
Lignins	5	20	20	20	5	5	20	20	5	20	5	20
Organic acids	5	2	2	2	5	5	2	2	5	2	5	2
Minerals (K, Ca, P, S)	8	4	4	4	8	8	4	4	8	4	8	4

<sup>&</sup>lt;sup>a</sup>See ref. 20; <sup>b</sup>See ref. 21; <sup>c</sup>see ref. 22; <sup>d</sup>see ref. 23; <sup>e</sup>Assumption; <sup>f</sup>see ref. 24.

Table S6. HHV of ethanol and biodiesel

	HHV, kJ/g
Biodiesel	37.7
Ethanol	29.7

See refs. 12 and 14.