Environ. Sci. Technol. **2007**, *41*, 1457−1464

# Life Cycle of the Corn−Soybean Agroecosystem for Biobased Production

AMY E. LANDIS,*
SHELIE A. MILLER, AND
THOMAS L. THEIS

*Institute for Environmental Science and Policy, University of Illinois at Chicago, Chicago, Illinois 60612*

Biobased product life cycle assessments (LCAs) have focused largely on energy (fossil fuel) usage and greenhouse gas emissions during the agriculture and production stages. This paper compiles a more comprehensive life cycle inventory (LCI) for use in future bioproduct LCAs that rely on corn or soybean crops as feedstocks. The inventory includes energy, C, N, P, major pesticides, and U.S. EPA criteria air pollutants that result from processes such as fertilizer production, energy production, and on-farm chemical and equipment use. Agroecosystem material flows were modeled using a combination of GREET (the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation model), a linear fractionation model that describes P biogeochemical cycling, and Monte Carlo Analysis. Results show that the dominant air emissions resulted from crop farming, fertilizers, and on-farm nitrogen flows (e.g., $N_2O$ and NO). Seed production and irrigation provided no more than 0.002% to any of the inventory emissions or energy flows and may be neglected in future LCAs of corn or soybeans as feedstocks from the U.S. Corn Belt. Lime contributes significantly (17% of total emissions) to air emissions and should not be neglected in bioproduct LCAs.

## Introduction

Agricultural life cycle assessments (LCAs) are becoming increasingly important with the growth of biofuels (i.e., biodiesel, ethanol) and biobased products (e.g., the biopolymers polyhydroxyalkanoate (PHA) and polylactic acid (PLA)) that have been driven by U.S. policies to reduce fossil fuel dependency (*1*). These bioproducts are often conceived as 'green' or environmentally friendly simply because the raw materials are plants as opposed to fossil fuels. It is possible for plant derived products to use more energy and emit more greenhouse gases than their fossil fuel counterparts, although this issue continues to be debated (*2, 3*). LCAs can help clarify such debates about the 'greenness' of biobased products and are a comprehensive way to inform decision-makers on the consequences of policy choices.

A LCA quantifies the environmental impacts of a product or process. Impact-minimizing LCAs provide information on which stage of production (creation, use, or disposal) is likely to cause the greatest environmental impact and may offer suggestions for minimizing those burdens throughout the product life. Comparative LCAs among possible products can help to determine the environmentally preferable alternative. Bioproduct LCAs, such as for biodiesel and PLA, can be compared to their petrobased counterparts, such as petrodiesel and polyethylene, to determine which products create more global warming, cause more eutrophication, or utilize fewer fossil fuels.

The body of research surrounding biobased production has focused largely on energy (fossil fuel) usage and greenhouse gas emissions during the agriculture and production stages, neglecting the consequences that the agricultural sector has on other nutrient cycles and material flows (*4*). For example, nitrogen and phosphorus are used extensively in agriculture and are the primary contributors to hypoxia and eutrophication in the U.S. (*5*, *6*). If biobased production were to require increasing amounts of land for nitrogen and phosphorus intensive crops, then associated environmental burdens such as hypoxia and eutrophication could be exacerbated. Environmental trade-offs involved in transitioning to bioproduction for commodity goods to reduce $CO_2$ emissions and fossil energy consumption have not been fully explored in biobased analyses. For example, aqueous emissions are often neglected entirely, while other EPA criteria air pollutants have been included in only a few projects. Such omissions become manifest in the impact assessment phase of LCA. Numerous Life Cycle Inventories (LCIs) and LCAs pertaining to agriculture and biobased products have been performed; most reflect only global warming and resource consumption with respect to the production of biobased materials, such as ethanol from corn and cellulosic matter (*7*), biodiesel from soybean crops (*8*), the biobased polymer PLA from corn (*9*), and the biopolymer polyhydroxyalkanoate (PHA) from genetically modified corn (*10*). Inventory compounds related to eutrophication, ecosystem quality, and human health impacts have been largely overlooked.

Inventory flows of environmental importance not only are solely limited to energy and carbon but also include N, P, pesticides, and air pollutants. Despite the fact that less than 5% of P fertilizers (usually triple super phosphate- $Ca(H_2PO_4)_2$) are transported through agricultural runoff as bioavailable (BioP) and soluble phosphorus (SP), aqueous P emissions have proven to be a significant contributor to eutrophication due to the sensitive nature of aquatic autotrophs to P enrichment (*5*). Nitrate in water bodies is responsible for acidification, eutrophication, and hypoxia, leading to a loss of biodiversity and natural habitats (*6*). Pesticides in runoff have been found to exceed maximum contamination levels in many areas of the U.S. and, in excess, are hazardous to human and/or ecological health (*11*). Air emissions from agricultural systems are also of concern with respect to human health. These emissions typically originate from the combustion of fuels and the application of fertilizer chemicals and cause a range of problems. Nitrogen oxides contribute to the formation of ground-level ozone and aerosols that cause respiratory illness and are one of the precursors to acid deposition (*6*, *12*). Sulfur dioxides and nitrogen oxides contribute to acidification and respiratory illness (*13*, *14*). Respiratory illnesses can also be caused by particulate matter, ammonia, and pesticides (*14−16*). Volatile organic compounds (VOCs) and nitrogen oxides contribute to smog formation (*17*).

This paper presents the agroecosystem material flows in the form of a LCI module created in conjunction with Monte Carlo Analysis (MCA) that can be used for future bioproduct LCAs relying on corn (*Zea mays* L.) or soybeans (*Glycine max* L.) as feedstocks. Life cycle material and energy flows associated with several agricultural operations have been

---

* Corresponding author phone: (312)996-1081; fax: (312)355-0760; e-mail: alandi1@uic.edu.

10.1021/es0606125 CCC: $37.00

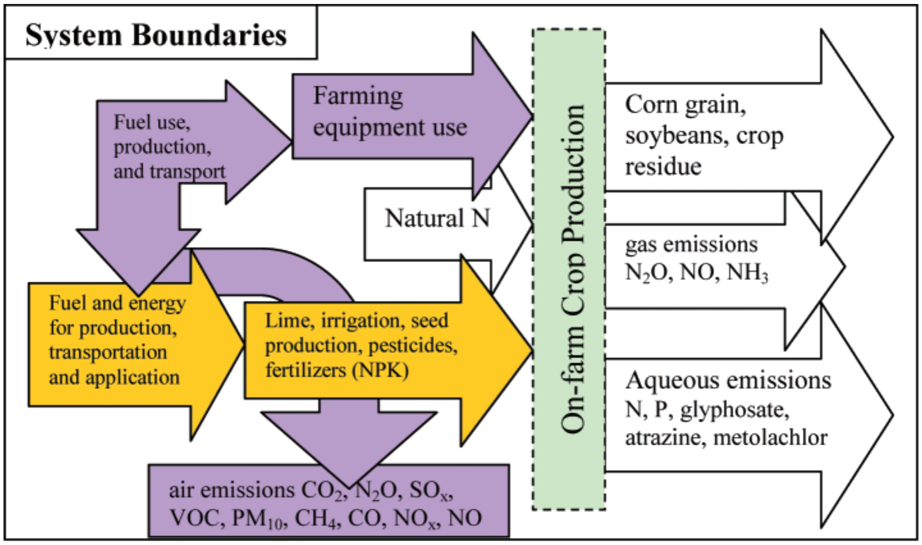

**FIGURE 1. System boundaries for the agroecosystem life cycle inventory (LCI). Flows in white are modeled via this study's methods. On-farm nitrogen flows are accounted for in previous work where natural N represents N fixation and soil N (*19*). Flows in purple are modeled in GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation model version 1.6 developed by Argonne National Labs). GREET is used to calculate all upstream emissions from fuel use, production, and transportation as well as the application of chemicals to agricultural fields. Flows in orange are modifications and additions to the GREET model and, unless otherwise specified, utilize GREET default assumptions.**

quantified in this study that are often omitted from analyses of biobased products, such as lime production and use, seed production, and irrigation. The inventory includes C, N, P, major pesticides, energy, and U.S. EPA criteria air pollutants resulting from agricultural processes. In this study, agroecosystem material flows were modeled using a combination of two models: an independently developed linear fractionation model that estimates P and pesticides lost from fields in runoff and the GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation) 1.6 Fuel-Cycle Model for Transportation Fuels and Vehicle Technologies developed by the Department of Energy that was used to estimate energy use, production, and transportation related to crop production as well as EPA criteria air emissions resulting from the combustion of those fuels (*18*). MCA was used in conjunction with LCA to incorporate the wide range of highly variable conditions associated with agricultural production. A detailed approach to modeling on-farm nitrogen cycling with MCA and the LCA approach has shown that MCA can be employed to account for the natural variability within agroecosystems in LCIs and can enhance the descriptiveness of LCI results when compared to traditional, single-valued LCA estimates (*19*).

## Methodology

**System Boundaries.** The agricultural system boundaries and material and energy flows accounted for in the LCI are depicted in Figure 1. The LCI was assessed for a corn−soybean rotation in the U.S. Corn Belt defined in a manner similar to that utilized by the National Corn Growers Association (NCGA) and the U.S. Department of Agriculture (USDA) as the top nine states producing 80% or more of the total U.S. corn and soybean production in 2003 (*20*, *21*). They include Iowa, Illinois, Nebraska, Minnesota, Indiana, Ohio, South Dakota, Wisconsin, and Missouri. Data collection was restricted to the period of 1990−2005. The corn−soybean rotation is examined as one system because approximately 80% of corn and soybeans are grown in rotation with each other, and nutrients are often shared between the rotated crops (*21*−*23*). The system boundaries in Figure 1 include material and energy flows upstream and downstream of the on-field crop production. Upstream emissions found on the left half of Figure 1, for example, include the energy and materials used during manufacture and transportation of fertilizers and fuels (however, the production of agricultural machinery or transport vehicles was not included in upstream calculations). Emissions downstream of the crop production are on the right half of Figure 1. Manure applied as fertilizer was excluded from this study since, on average, only 18% of corn crops and 6% of soybean crops receive manure as a fertilizer supplement to synthetic fertilizers (*21*−*23*). Most farmers applying manure adjust the levels of synthetic fertilizers applied so that the total nitrogen applied is only slightly higher than those farms applying solely synthetic fertilizers (*21*). A description of the models used to develop the LCI is given in Table 1; the models are discussed in more detail in the following sections.

**GREET 1.6 Model.** The GREET 1.6 Model was utilized in this study for compiling a LCI of on-farm and upstream energy use and air emissions (*18*). These flows include energy used to operate farming equipment, energy used for transportation of fertilizers and other agricultural materials, and energy used during the production of agricultural chemicals. GREET also calculates the energy required to produce various types of fuels such as coal, electricity, natural gas, diesel, and residual oil. The energy estimates are aggregated into total energy, fossil fuel, and petroleum consumption for the various agricultural processes which include the following: crop farming; fertilizer production, transportation, and application; transportation of crops to milling facilities; and pesticide production, transportation, and application. Criteria EPA air emissions, such as VOCs, carbon monoxide, nitrogen oxides, particulate matter, sulfur oxides, carbon dioxide, methane, and nitrous oxide, are calculated in GREET based upon emission factors from EPA databases (*24*). For the corn and soybean rotations, all reported data (unless otherwise noted) utilize GREET 1.6 default assumptions and probability distributions associated with near-term technologies.

**Model Uncertainty and Variability.** MCA was used to assess the uncertainty and variability in association with GREET and in the downstream emissions fractionation model. The GREET 1.6 model contains data pertaining to the variability and uncertainty of energy production and the resultant emissions which can be accessed with the Crystal

**TABLE 1. Models Used To Create the Life Cycle Inventory**

| | fertilizers | corn farming | transportation | pesticides | lime, seed production, irrigation |
|---|---|---|---|---|---|
| **default GREET 1.6**[a] (energy and air emissions) purple flows in Figure 1 | N (average of $NH_3$, urea, and $NH_4NO$), $P_5O_2$, and $K_2O$: energy required for production, transportation, and application | fuels used on field for corn farming operations | transportation of corn, soybeans, and agricultural chemicals (each with different distances and modes of transport) | Generic insecticides. General herbicides calculated from percentage applied to each crop of atrazine, acetochlor, metolachlor, and cyanazine. Energy use for production, transportation, and application. | |
| **modified GREET 1.6** (energy and air emissions) orange flows in Figure 1 | N, P, K application rates modified, factors added to reflect the percentage of crops that receive each chemical | all default GREET assumptions used | all default GREET assumptions used | All application rates modified, factors added to reflect the percentage of crops that receive each chemical. Corn: original data from GREET 1.6 used for atrazine, metolachlor, acetochlor, and insecticides. Soy: Glyphosate added as the only pesticide (no insecticide application). | Energy used to produce aglime ($CaCO_3$) and seeds (excluding farming). Energy used to transport and apply lime and seeds estimated based on default GREET assumptions for other ag chemicals (i.e., N, P, K, herbicides). Energy used for irrigation. |
| **fractionation model** (runoff)[b] white flows in Figure 1 | N and P runoff: loss from fields as a function of application rate | | | atrazine, metolachlor, and glyphosate runoff: loss from fields as a function of application rate | |

[a] The GREET 1.6 model estimates the upstream energy required to produce basic fuels such as electricity, coal, natural gas, gasoline, diesel, and residual oil and subsequently aggregates these energy uses to an estimate of total energy based on low heating values. GREET 1.6 also calculates air emissions associated with the use of the total energy (including air emissions from upstream energy use) based on EPA emission factors. [b] The nitrogen flows on-field ($N_2O$, NO, $NH_3$ air emissions, and $NO_3^-$ in runoff) were estimated by Miller et al. (*19*).

**TABLE 2. Model Equations**[a]

| eq no. | description | equation |
|---|---|---|
| 1 | input load | $L_{x,i}^{in} = R_{xi}\cdot f_{x,i}^{treated}\cdot Y_i^{-1}$ |
| 2 | irrigation | $E_{I,i} = E_I\cdot f_{I,i}\cdot f_I\cdot Y_i^{-1}$ |
| 3 | seed production, packaging and distribution | $E_{s,i} = E_S\cdot W_{S,i}\cdot R_{S,i}\cdot Y_i^{-1}$ |
| 4 | lime production and transportation | $E_{L,i} = (E_L^{transport} + E_L^{prodn})\cdot R_L\cdot f_L^{treated}\cdot CR_i\cdot Y_i^{-1}$ |
| 5 | corn crop rotation (CR) | $CR_{corn} = a_{corn}\cdot(a_{corn} + a_{soy})^{-1}$ |
| 6 | soybean crop rotation (CR) | $CR_{soy} = a_{soy}\cdot(a_{corn} + a_{soy})^{-1}$ |
| 7 | glyphosate | $E_{glyp,soy} = (E_{glyp,soy}^{transport} + E_{glyp,soy}^{prodn})\cdot L_{glyp,soy}^{in}$ |
| 8 | load in runoff | $L_{x,i}^{runoff} = L_{x,i}{}^{in}\cdot f_{x,i}^{runoff}$ |

[a] Parameter definitions: (all loads (L), rates (R), and yields (Y) are on a per year basis) $x$ = *P*, *K*, *glyp*hosate, *acet*ochlor, *atraz*ine, *met*olachlor, *insect*icides general; $i$ = crop type (*corn* or *soy*beans); $L_{x,i}^{in}$ = normalized input load (kg $x$/kg crop $i$ harvested); $R_{x,i}$ = rate of application (kg $x$/ha for crop $i$); $f_{x,i}^{treated}$ = fraction of crop $i$ treated with $x$; $Y_i$ = yield (kg $i$/ha); $E_{x,i}$ = normalized energy use (MJ $x$ /kg crop $i$ harvested) ($x$ = *L*ime, *S*eed, or *I*rrigation); $E_x^{transport}$ = energy required for transportation of $x$ (lime or glyphosate) (MJ/kg $x$); $E_L^{prodn}$ = energy required to mine, produce, and apply lime (MJ/kg lime); $R_S$, $R_L$ = rate of application (kg seeds or lime/ha); $f_L^{treated}$ = fraction of crops (both corn and soy) treated with *L*ime; $CR_i$ = crop rotation for crop $i$ (*corn* or *soy*beans); $a_i$ = acres of crop $i$ planted calculated from 1990 to 2003; $E_S$ = energy required to produce (not including farming and harvesting), package, and distribute seeds; $W_{S,i}$ = weight of seeds for crop $i$ (kg/seed); $E_I$ = energy required for operating pump to irrigate crops; $f_{I,i}$ = fraction of irrigated land per total farmland for crop $i$; $f_I$ = fraction of irrigated land that utilizes energy; $E_{glyp,soy}^{prodn}$ X = energy required to produce glyphosate (MJ/kg glyphosate); $L_{x,i}^{runoff}$ = normalized load of $x$ contained in surface runoff (kg $x$/kg crop $i$ harvested); $f_{x,i}^{runnoff}$ = fraction that was applied of $x$ that is contained within runoff for crop $i$.

Ball version 5.5 software (*25*). A probability distribution and range of values are assigned in GREET for each parameter. Probability distributions added within GREET modifications were chosen based on a best-fit regression using the Chi-squared test for parameters that have large data sets (20 or greater points). Parameters with single or two data points were assigned uniform distributions; parameters with three points were assigned triangular distributions; and parameters with data sets less than 20 points were assigned distributions based on expert judgment informed by statistical analysis (i.e., mean, standard deviation) calculated from the data available.

**GREET Modifications.** Three major modifications were made to GREET to enhance the level of detail of the upstream model: additions to the application rates of agricultural chemicals, changes in the types of pesticides modeled, and the addition of several new inputs to the GREET agricultural system including lime, seed production, irrigation, and the pesticide glyphosate [*N*-(phosphonomethyl) glycine]. In the first modification, application rates for fertilizer and pesticides (the term pesticide includes herbicides and insecticides) applications were altered to reflect the practices within the Corn Belt. GREET uses an application rate *R* (mass of *x*/area) for chemical inputs, the assumption being that all crops are treated with chemical *x*. The modified model incorporates the fraction of crops *f* in the Corn Belt that is treated with chemical *x* (eq 1). Probability distributions were included for each of the parameters in Table 2. The distribution parameters and sources used to create the probability distributions are outlined in the Supporting Information for all modified inputs including synthetic phosphorus, nitrogen, and potassium fertilizers as well as atrazine (2-chloro-4-

ethylamino-6-isopropylamino-1,3,5-triazine), metolachlor [2-chloro-*N*-(2-ethyl-6-methyl-phenyl)-*N*-(methoxy-1-methylethyl) acetamide], acetochlor [2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl) acetamide], and glyphosate pesticides.

In the second modification, changes were made to the types of pesticides modeled. GREET 1.6 employs two general categories for pesticides: herbicides and insecticides. The model does delineate specific data for the production of atrazine, acetochlor, metolachlor, and general insecticides. These individual chemical data were used within this LCI. The modified model included the assumption that atrazine, acetochlor, and metolachlor were applied only to corn crops. Insecticide application rates and upstream energy usage are also calculated only for corn crops based on the default GREET methods since insecticide application was assumed to be negligible within this study for soybean production (less than 3% of soybean crops within the Corn Belt receive insecticides, compared to approximately 28% of corn crops (*26*, *27*)). Likewise, fungicides were not included in any calculations because they are applied to less than 1% of both crops (*26*, *27*). Components whose fraction of total mass is below the 5% cutoff are excluded in the interests of analytical tractability (*28*).

The third modification incorporated several new inputs to the GREET 1.6 agricultural model including irrigation; seed production and application; lime production, transportation, and application; and the production, transportation, and application of the soybean specific herbicide glyphosate. Irrigation was accounted for only on corn crops (approximately 14% of corn crops are irrigated with pumps in comparison with 5% of soybean crops (*21*, *29*)). Energy use data for irrigation (eq 2) include only the energy required to pump irrigation groundwater; surface water is applied primarily through gravitational powered irrigation and is considered to be negligible in terms of energy requirements (*29*, *30*). The emissions and energy used during seed production and application were also added to GREET. The energy used during seed production was assumed to be the same for both corn and soybean seeds. Seed production energy was previously estimated from seed prices and U.S. Office of Technology dollar-to-energy conversion factors for general agricultural products (*30*, *31*). The energy data represent production, packaging, and distribution of seeds but do not include growing and harvesting. Equation 3 was used in the modified model to calculate energy use for seed production in GREET from the rate $R$ of seed application, the weight $W$ of seeds, and the energy $E_S$ required to produce, package, and distribute seeds.

The final two additions to the GREET model were lime and glyphosate. Agricultural lime (aglime) is frequently used to decrease the acidity of agricultural soils. The energy required to produce, transport, and apply lime has been added to GREET (eq 4) to calculate the resultant emissions from the energy consumption. The energy use during production and application $E_L^{prodn}$ was obtained from West and Marland (*30*), but their data had no reported uncertainty or probability information and were therefore used as single-value estimates with no associated range. Lime was assumed to be applied independently of the crop type. The crop rotation parameter, $CR$, is used in eq 4 to allocate the energy used to produce lime on a mass basis between the crops based on the acreage planted, as described by eqs 5 and 6. Glyphosate is primarily used as an herbicide for soybean crops (*26*) and was also added to the GREET model. The production energy for glyphosate $E_{glyp,soy}^{prodn}$ was obtained from the ecoinvent database and is defined in the Supporting Information (*32*). The energy use for transportation of lime $E_L^{transport}$ (eq 4) and glyphosate $E_{glyp,soy}^{transport}$ (eq 7) and the resultant emissions from the fuel usage were modeled using GREET's original agricultural chemical assumptions. GREET assumes that each agricultural chemical (N, P, and K fertilizers as well as pesticides and insecticides) undergoes the same mode of transportation (50% by barge and 50% by rail) and distance (400 miles by barge and 750 miles by rail).

**Fractionation Model.** Aqueous emissions downstream of the agricultural system (depicted in Figure 1) were calculated independently of GREET via a fractionation approach with MCA. This approach was reported in earlier work for agricultural nitrogen flows (*19*). Equation 8 describes the amount of chemical lost from fields in runoff $L_{x,i}^{runoff}$, which is calculated as the fraction of chemical lost with respect to the total mass of chemical that was applied to a crop. The agricultural chemicals modeled in surface runoff include both BioP and SP (excluding P from tile drainage) as well as runoff from surface and tile drainage for glyphosate, atrazine, and metolachlor. The fate of pesticides in soils, water, and plant matter is more complex because of differing degradation products and rates that vary by local conditions. This model does not attempt to model such interactions but rather to utilize LCI in conjunction with MCA to represent the possible range of pesticides in runoff. Phosphorus also partitions into various parts of the agricultural system. The only input to the system considered in this model was synthetic phosphorus fertilizer (PF), which was calculated based on eq 1. It was assumed that no soil-P was available from the previous year as an input since P quickly becomes immobilized and biologically unavailable (*5*). Phosphorus inputs from the air (deposition), rain, and wind erosion are negligible and were not accounted for. Partitioning of P within the system creates two major outputs of concern: P contained in plant matter as well as BioP and SP lost within runoff. Biologically unavailable P is also commonly lost from the agricultural system within erosion and was not considered in this model (*33*, *34*). It was assumed that no residues (i.e., stalks) were removed and that the P contained within the residues joins the soil fractions.

**Allocation.** While allocation was conducted on a mass-based allocation to individual crops normalized per year throughout the analysis, certain flows such as lime cannot be allocated so simply due to the nature of the corn−soybean rotation. Allocation has varied within previous LCAs, from allocation according to the crop of application, to the uptake efficiency, and to the percentage of total land used in the cropping plan (*35*). All emissions and energy use are allocated 100% to the corn grain or soybean on a mass basis, since the boundaries of the LCI end before the milling phase. Impacts due to pesticide use, production, and transportation are allocated wholly to the crop for which they are intended. Glyphosate related emissions were allocated solely to soybeans since this pesticide is applied to 80% of soybean crops, and the remaining 16% of soybeans receive a mix of over 30 different pesticides (*26*). Atrazine, metolachlor, and acetochlor related emissions were allocated solely to corn during the rotation because they were consistently the top three herbicides applied to corn crops in the U.S. Corn Belt within the modeled years. In practice, lime is applied based on soil needs (independently of the crop type) and may be utilized for either corn or soybeans since they both require soil with the same pH range of 6.0−6.5 (*36*). The upstream emissions from production, transportation, and application of lime are dependent on the amount of time a crop spends on the soil in rotation *CR*. Crops are not consistently rotated on a biannual or annual basis. Lime is therefore allocated based on the annualized mass applied as a function of the crop rotation, which is represented as a fraction of the acreage planted for each crop in the Corn Belt described in eqs 4−6.

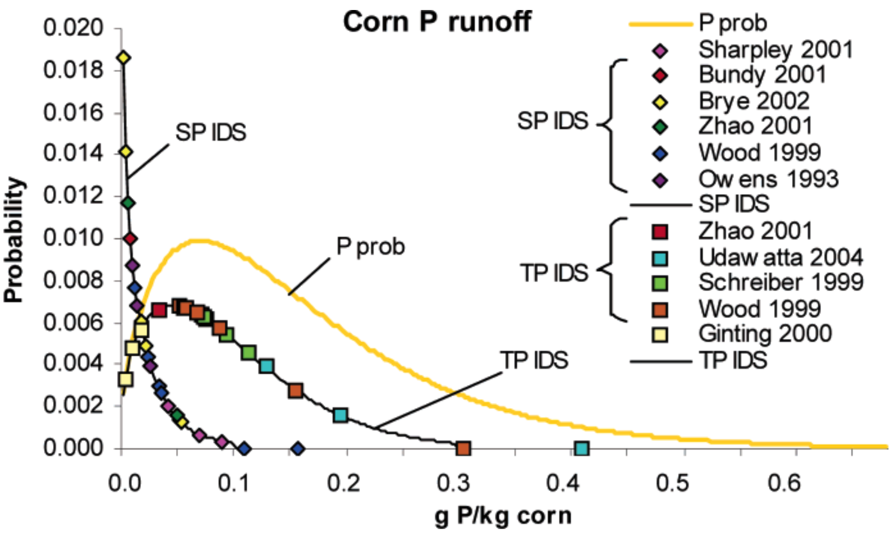

**FIGURE 2. Corn P runoff probability distribution compared to independent data sets (IDSs). Probability distribution for corn P runoff (P prob) was calculated using Monte Carlo Analysis from runoff of soluble P (SP) and bioavailable P (BioP) and is compared to two types of IDSs: SP and total P (TP). Various agricultural conditions are represented in the individual sources including the following: various soil types; runoff from synthetic fertilizer inputs (*37*–*39*); tilling practices such as no till (NT), chisel plow, paraplow, and shallow till (*40*–*44*); and P leaching included from crop residues (*45*). Best fit distribution type, mean ($\mu$), standard deviation ($\sigma$), and total number of data points are reported for both the modeled probable P emissions and IDSs. P prob distribution: gamma, $\mu = 0.17$, $\sigma = 0.19$; SP IDS weibull, $\mu = 0.024$, $\sigma = 0.031$, 52 data points; TP IDS weibull, $\mu = 0.098$, $\sigma = 0.10$, 22 data points**

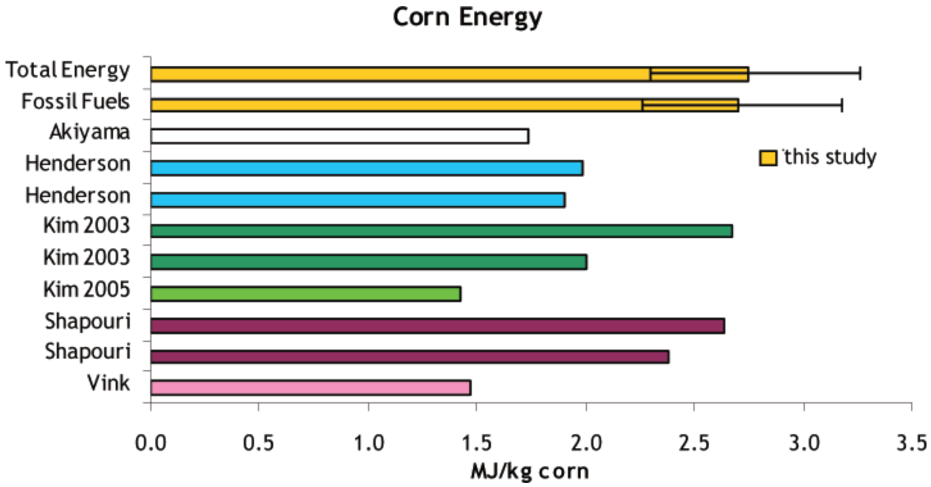

**FIGURE 3. Corn energy use. The range estimated within this study is compared to previous studies. The previous studies for total energy use include single-value estimates from LCAs of bioproducts (*7*, *9*, *10*, *46*, *47*) with studies solely of agricultural $CO_2$ fluxes and energy consumption (*30*, *48*, *49*). The Vink (2003) comparison point is roughly estimated from a conversion of 0.28 kg PLA/kg corn from references external to the original source (*50*–*52*).**

## Results and Discussion

This study integrates important material and energy flows into the corn–soybean agricultural inventory. With the use of a fractionation model to assess aqueous emissions and GREET to quantify air emissions, a comprehensive LCI for the corn–soybean agroecosystem has been compiled that is representative of the U.S. Corn Belt. The inventory data are given in the Supporting Information (Table B) with the parameters contributing to the uncertainty and variance of the mean for each flow; these sensitivity parameters do not influence the magnitude of the mean.

The fractionation approach to modeling agroecosystem chemical flows for use in LCA was corroborated in this study by comparison of the model results to independent data sets (IDSs). While this approach has been presented and validated in previous work (*19*), it is examined again for P flows estimated within this study. The independent data sets were collected separately from the data used to estimate the probable P emissions and are representative of two different types of P: soluble P (SP IDS) and total P (TP IDS). The probable range of values representing aqueous P runoff from corn fields in the Corn Belt is shown in Figure 2 as 'P prob' and was estimated using MCA to repeatedly and randomly sample values from the assigned distributions for each parameter in eq 8. Figure 2 shows that the most likely value estimated is approximately 0.1 g P emissions per kg of corn grain with a possible range of values extending from 0 to 0.65 g P/kg corn. The simulated P runoff was modeled from SP and BioP data and captures a wide range of P emissions. The TP IDS agrees well with the range estimated in this study. The wide range of P runoff estimated by the LCI-MCA model can be attributed to the parameter $f_{P,i}^{runoff}$ which contributes to 57% of the P variance and uncertainty for corn crops and 90% for soy crops. The $f_{P,i}^{runoff}$ parameters have high variability because they reflect a wide variety of conditions across the Corn Belt.

The remaining inventory was also compared to IDSs, where data permitted, to further validate the model results.

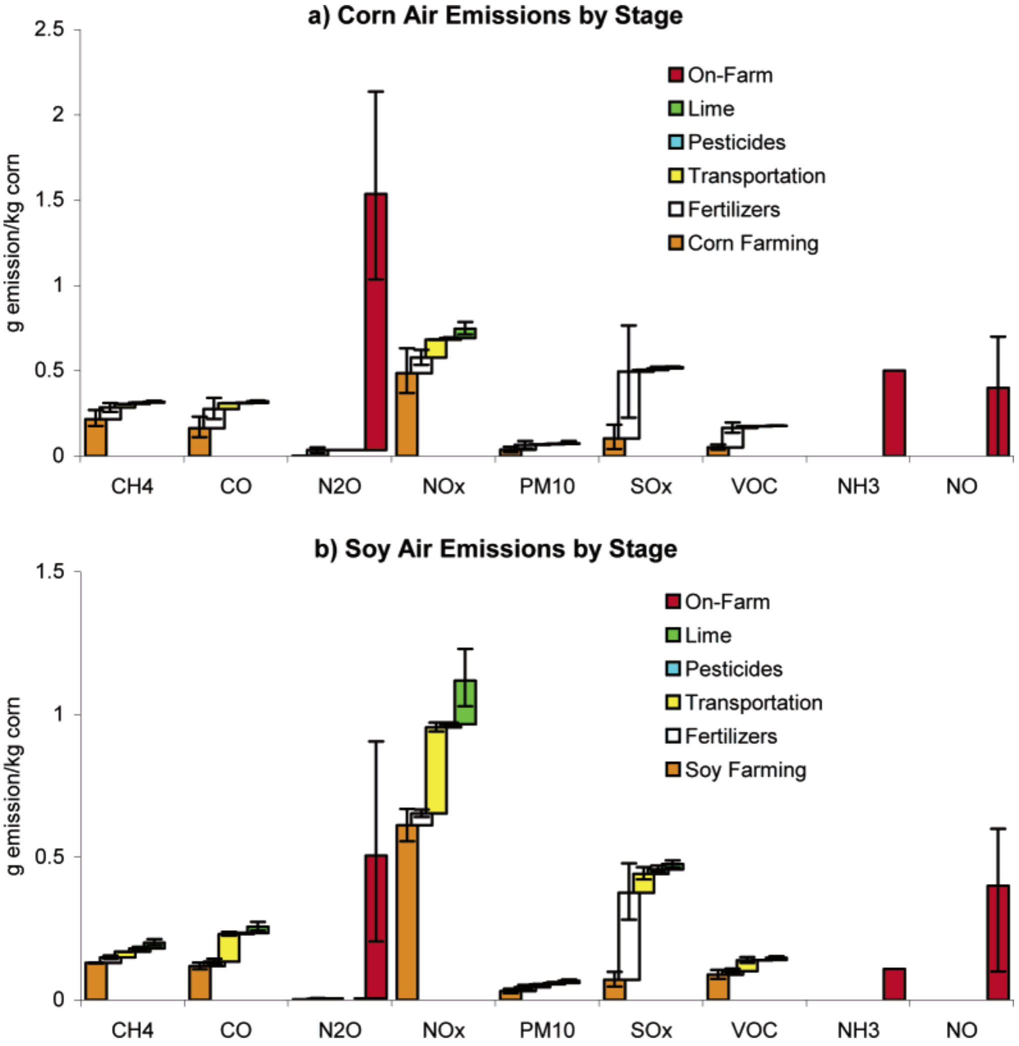

**FIGURE 4. (a) and (b). Air emissions by stage as modeled in GREET 1.6, *corn farming* and *soy farming* include the operation of machinery during farming but not the creation of the machinery. *Fertilizers* include the production, transportation, and application of N, P, and K fertilizers. *Transportation* represents the transportation of the crop to the mill. *Pesticides* include the production, transportation, and application of all pesticides applied to each crop. *Lime* represents the production, transportation, and application of lime as a soil amendment. *On-Farm* represents the emissions that take place directly from the field, such as ammonia volatilization and nitrification and denitrification of NO and $N_2O$. *On-Farm* data are taken from ref *19*. The mean estimated within this study is presented in the bar graph. Certainty bars are the 10 and 90% confidence intervals from the MCA. Urban emissions are included.**

While there is extensive literature on agrochemicals in runoff, load data alone are compatible for comparison with this model. Estimates from both the fractionation model and GREET proved to accurately describe the same range of possible soy P, atrazine, metolachlor, and corn $CO_2$ emissions as was found in the IDSs. Twenty-one different studies were used to construct IDSs for comparison to P, atrazine, and metolachlor runoff as well as total energy use and $CO_2$ emissions; the figures of which are presented in the Supporting Information. Independent observations of EPA criteria pollutants and glyphosate were not abundant enough to make an appropriate comparison.

The principal discrepancy between estimates from this model and IDSs is for energy use, depicted in Figure 3. These differences are attributable to the difference between the original GREET and the modified GREET models and to dissimilar definitions of LCI system boundaries between this model and IDSs (previous studies), exemplifying the importance of including lime and crop-appropriate herbicides within biobased LCAs. The probable range of total energy used encompasses previous estimates but shows roughly 40% probability that energy use may also be higher (*46*). Previous studies include upstream energy use but do not attribute energy due to lime or glyphosate to soy crops. For corn crops, the different amounts of diesel, gasoline, liquid petroleum gas, electricity, and natural gas for corn farming can differ between previous studies and this work by 430−520 kJ/kg of crop with respect to total energy use. Many of the other single-value LCA estimates in Figure 3 derive their energy use from similar GREET 1.5 data and show similar discrepancies when compared to this approach (*7*, *10*, *46*).

Single-valued LCAs not derived from GREET exhibit energy use estimates on the lower end of the probable range because of different selections of boundary conditions, inventory, and inputs. Vink et al. (*9*) provide $CO_2$, fossil fuel usage, and water use for dedicated corn grown near their Blair, Nebraska facility for their LCA of PLA. Their inputs include energy use by the farmer in the form of natural gas, diesel, propane, and gasoline, and corn growing operations including seed production, 'fertilizers,' irrigation water, 'pesticides,' and corn transportation to a milling facility. The inclusion of upstream energy could add approximately 1100 kJ/kg of corn to Figure 3. Adding the energy associated with lime production and application would add at least 54 kJ/kg corn. The addition of these flows plus agricultural chemical production and application would bring the Vink 2003 estimate well within range of the most probable value estimated within this study. The single point comparison from Henderson (*47*) in Figure 3 represents a LCA for ethanol production in Ontario. Inputs include energy for planting, fertilizing, spraying, harvesting, and drying corn as well as the energy required to manufacture fertilizers and pesticides. Lime was assumed to have a zero kg per hectare application rate. The energy attributed to field operations, fertilizers, and pesticides are all lower than the probable mean total energy use in Figure 3, with a difference of 1000 kJ/kg of corn attributed to field operations alone.

Certain activities within the agroecosystem have significant effects on the magnitude of the resultant emissions. The LCI air emissions for corn and soybean production are represented by type of activity or stage of agricultural production in Figure 4. The inventory is presented in different functional units, is not weighted, and therefore is not commensurate or meant to be directly compared. The LCI documents material (mass of emission per kg of crop) and energy (joule per kg crop) flows which occur within the system boundaries (a life cycle impact assessment (LCIA) characterizes and assesses the environmental effects using the data obtained from the inventory). Emissions from vehicle and machine operations (i.e., the combustion of diesel and gasoline) result in high $NO_x$ from crop farming and lime (which is attributed primarily to lime transportation). Lime contributes significantly (17% of the total emissions) to $NO_x$ emissions in soy production and should not be neglected in bioproduct LCAs. On-farm emissions of N compounds also significantly affect the inventory; they make up 96% of corn and 99% of soy $N_2O$ emissions while also adding $NH_3$ and NO, compounds not estimated in GREET, to the inventory. While lime and glyphosate proved to be important agrochemicals to consider in bioproduct LCAs, irrigation and seed production contributed minimally (e.g., less than 0.002% to total energy) to the inventory and can be neglected from future bioproduct LCAs relying on corn or soybeans as feedstocks.

GREET 1.6 allows for a distinction to be drawn between urban and nonurban air emissions for CO, $NO_x$, $PM_{10}$, $SO_x$, and VOCs. The urban and nonurban air emissions have been combined in the LCI presented in Figure 4. Urban emissions contribute relatively insignificantly to the corn emissions, with urban $SO_x$ supplying the highest at 5.2% percent of all $SO_x$ emissions and urban $PM_{10}$ providing the lowest at 2.3% of $PM_{10}$ emissions. Soybean urban emissions, however, constitute an important fraction with urban VOCs making up 25% of the total, CO with 23%, $SO_x$ with 16%, $NO_x$ with 15%, and $PM_{10}$ with 12% of the respective emissions.

The agricultural inventory presented and validated within this paper can be used for future bioproduct LCAs relying on corn or soybeans as feedstocks. Variability and uncertainty can be carried through the remainder of the bioproduct LCA with the use of MCA and the probability data presented within the inventory. As with any LCA, practitioners must judiciously choose allocation methods, system boundaries, and inventory items. While the inventory presented in this paper may not be completely comprehensive, it does provide a rich set of data that could enhance the LCA of biobased products with the inclusion of nutrient exports from agriculture such as nitrogen and phosphorus.

## Acknowledgments

The authors acknowledge the following funding: NSF IGERT (Integrative Graduate Education and Research Traineeship Program) Grant DGE 9870646 and NSF Biocomplexity in the Environment MUSES (Materials Use: Science, Engineering, and Society) Grant DMI-0329359. We thank Thomas Seager, Susan Powers, and Michael Wang for their helpful advice and guidance.

## Supporting Information Available

Tabular input data used to develop the model, including application rates, energy use, model distributions, and references; tabular inventory results; energy use by stage calculated from GREET; and comparison between probable range estimated within this study and previous studies for soybean P runoff, metolachlor runoff, atrazine runoff, and corn $CO_2$ emissions. This material is available free of charge via the Internet at http://pubs.acs.org.

## Literature Cited

(1) DOE. USDA Vision for Bioenergy & Biobased Products in the United States. Biomass Technical Advisory Committee, Biomass R&D Act of 2000, 2002.

(2) Kurdikar, D.; Fournet, L.; Slater, S. C.; Paster, M.; Gerngross, T. U.; Coulon, R. Greenhouse gas profile of a plastic material derived from a genetically modified plant. *J. Ind. Ecol.* **2000**, *4*, 107−122.

(3) Scott, G.; Wiles, D. M. Programmed-life plastics from polyolefins: a new look at sustainability. *Biomacromolecules* **2001**, *2*, 615−622.

(4) Landis, A. E.; Theis, T. L. Response to 'Comments on Workshop Report on the Economic and Environmental Impacts of Biobased Production'. *Int. J. Life Cycle Assess.* **2006**, *11*, 213−214.

(5) Smil, V. Phosphorus in the Environment: Natural Flows and Human Interferences. *Annu. Rev. Energy Environ.* **2000**, *25*, 53−88.

(6) Galloway, J. N.; Aber, J. D.; Erisman, J. W.; Seitzinger, S. P.; Howarth, R. W.; Cowling, E. B.; Cosby, B. J. The Nitrogen Cascade. *BioScience* **2003**, *53*, 341−356.

(7) Shapouri, H.; Duffield, J. A.; Wang, M. *The Energy Balance of Corn Ethanol: An Update*; U.S. Department of Agriculture, Economic Research Service: 2002.

(8) Lave, L.; MacLean, H.; Hendrickson, C.; Lankey, R. Life-Cycle Analysis of Alternative Automobile Fuel/Propulsion Technologies. *Environ. Sci. Technol.* **2000**, *34*, 3598−3605.

(9) Vink, E. T. H.; Rabago, K. R.; Glassner, D. A.; Gruber, P. R. Applications of life cycle assessment to NatureWorks polylactide (PLA) production. *Polym. Degrad. Stab.* **2003**, *80*, 403−419.

(10) Akiyama, M.; Tsuge, T.; Doi, Y. Environmental life cycle comparison of polyhydroxyalkanoates produced from renewable carbon resources by bacterial fermentation. *Polym. Degrad. Stab.* **2003**, *80*, 183−194.

(11) Shipitalo, M. J.; Owens, L. B. Atrazine, Deethylatrazine, and Deisopropylatrazine in Surface Runoff from Conservation Tilled Watersheds. *Environ. Sci. Technol.* **2003**, *37*, 944−950.

(12) Howarth, R. W.; Boyer, E. W.; Pabich, W. J.; Galloway, J. N. Nitrogen Use in the United States from 1961−2000. and Potential Future Trends. *AMBIO* **2002**, *31*, 88−96.

(13) Dupont, J.; Clair, T. A.; Gagnon, C.; Jeffries, D. S.; Kahl, J. S.; Nelson, S. J.; Peckenham, J. M. Estimation of Critical Loads of Acidity for Lakes in Northeastern United States and Eastern Canada. *Environ. Monit. Assess.* **2005**, *109*, 275−292.

(14) Filleul, L.; Rondeau, V.; Vandentorren, S.; Le Moual, N.; Cantagrel, A.; Annesi-Maesano, I.; Charpin, D.; Declercq, C.; Neukirch, F.; Paris, C.; Vervloet, D.; Brochard, P.; Tessier, J. F.; Kauffmann, F.; Baldi, I. Twenty five year mortality and air pollution: Results from the French PAARC survey. *Occup. Environ. Med.* **2005**, *62*, 453−460.

(15) Beard, J.; Sladden, T.; Morgan, G.; Berry, G.; Brooks, L.; McMichael, A. Health impacts of pesticide exposure in a cohort of outdoor workers. *Environ. Health Perspect.* **2003**, *111*, 724−730.

(16) Kirkhorn, S. R.; Garry, V. F. Agricultural lung diseases. *Environ. Health Perspect.* **2000**, *108*, 705−712.

(17) Jenkin, M. E.; Hayman, G. D. Photochemical ozone creation potentials for oxygenated volatile organic compounds: sensitivity to variations in kinetic and mechanistic parameters. *Atmos. Environ.* **1999**, *33*, 1275−1293.

(18) Wang, M. Q. *GREET-Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation, version 1.6*; Department of Energy, Argonne National Laboratory: Argonne, IL, 2005.

(19) Miller, S. A.; Landis, A. E.; Theis, T. L. Use of Monte Carlo Analysis to Characterize Nitrogen Fluxes in Agroecosystems. *Environ. Sci. Technol.* **2006**, *40*, 2324−2332.

(20) USDA. *Corn for Grain 1995: Yield per harvested acres by county*; USDA National Agricultural Statistics Service: 2003. http://www.usda.gov/nass/graphics/county95/cryld.htm (accessed Nov 2003).

(21) USDA. *Crop production practices data*; USDA Economic Research Service: Agricultural Resource Management Survey, 2001.
(22) Christensen, L. A. *Soil, Nutrient, and Water Management Systems Used in U.S. Corn Production*; USDA, Economic Research Service: Agriculture Information Bulletin No. 774; 2002.
(23) Padgitt, M.; Newton, D.; Penn, R.; Sandretto, C. *Production Practices for Major Crops in U.S. Agriculture, 1990−97*; USDA, Economic Research Service: Statistical Bulletin No. 969; 2000.
(24) USEPA. *Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources*; United States Environmental Protection Agency: 1995.
(25) Decisioneering, Inc. *Crystal Ball, version 5.5*; London, 2003.
(26) USDA. *Agricultural Chemical Usage: 2002 Field Crops Summary*; USDA National Agricultural Statistics Service: 2003.
(27) USDA *Agricultural Chemical Usage: 2000 Field Crops Summary*; USDA National Agricultural Statistics Service: 2001.
(28) Graedel, T. E. *Streamlined Life-Cycle Assessment*; Prentice Hall: Upper Saddle River, 1998.
(29) USDA. *1997 Census Of Agriculture*; National Agricultural Statistics Service: 1999.
(30) West, T. O.; Marland, G. A synthesis of carbon sequestration, carbon emissions, and net carbon flux in agriculture: Comparing tillage practices in the United States. *Agric., Ecosyst. Environ.* **2002**, *91*, 217−232.
(31) Borjesson, P. I. I. Energy analysis of biomass production and transportation. *Biomass Bioenerg.* **1996**, *11*, 305−318.
(32) ecoinvent Centre. *Ecoinvent data v1.1*; Final reports ecoinvent 2000 No. 1-15; Swiss Centre for Life Cycle Inventories: Dübendorf, 2004, CD-ROM.
(33) Becher, K. D.; Schnoebelen, D. J.; Akers, K. K. B. Nutrients discharged to the Mississippi River from Eastern Iowa Watersheds. *J. Am. Water Resour. Assoc.* **2000**, *36*, 161−173.
(34) Moog, D. B.; Whiting, P. J. Climatic and agricultural factors in nutrient exports from two watersheds in Ohio. *J. Environ. Qual.* **2002**, *31*, 72−83.
(35) van Zeijts, H.; Leneman, H.; Wegener, Sleeswijk, A. Fitting fertilisation in LCA: allocation to crops in a cropping plan. *J. Cleaner Prod.* **1999**, *7*, 69−74.
(36) Vitosh, M. L.; Johnson, J. W.; Mengel, D. B. *Tri-state fertilizer recommendations for corn, soybeans, wheat and alfalfa*; Michigan State University, The Ohio State University, and Purdue University: Extension Bulletin E-2567; 1995.
(37) Sharpley, A. N.; McDowell, R. W.; Weld, J. L.; Kleinman, P. J. A. Assessing Site Vulnerability to Phosphorus Loss in an Agricultural Watershed. *J. Environ. Qual.* **2001**, *30*, 2026−2036.
(38) Zhao, S. L.; Gupta, S. C.; Huggins, D. R.; Moncrief, J. F. Tillage and nutrient source effects on surface and subsurface water quality at corn planting. *J. Environ. Qual.* **2001**, *30*, 998−1008.
(39) Wood, B. H.; Wood, C. W.; Yoo, K. H.; Yoon, K. S.; Delaney, D. P. Seasonal surface runoff losses of nutrients and metals from soils fertilized with broiler litter and commercial fertilizer. *J. Environ. Qual.* **1999**, *28*, 1210−1218.
(40) Bundy, L. G.; Andraski, T. W.; Powell, J. M. Management Practice Effects on Phosphorus Losses in Runoff in Corn Production Systems. *J. Environ. Qual.* **2001**, *30*, 1822−1828.
(41) Brye, K. R.; Andraski, T. W.; Jarrell, W. M.; Bundy, L. G.; Norman, J. M. Phosphorus Leaching under a Restored Tallgrass Prairie and Corn Agroecosystems. *J. Environ. Qual.* **2002**, *31*, 769−781.
(42) Udawatta, R. P.; Motavalli, P. P.; Garrett, H. E. Phosphorus loss and runoff characteristics in three adjacent agricultural watersheds with claypan soils. *J. Environ. Qual.* **2004**, *33*, 1709−1719.
(43) Owens, L. B.; Edwards, W. M. Tillage studies with a corn-soybean rotation: surface runoff chemistry. *Soil Sci. Soc. Am. J.* **1993**, *57*, 1055−1060.
(44) Ginting, D.; Moncrief, J. F.; Gupta, S. C. Runoff, solids, and contaminant losses into surface tile inlets draining lacustrine depressions. *J. Environ. Qual.* **2000**, *29*, 551−560.
(45) Schreiber, J. D. Nutrient leaching from corn residues under simulated rainfall. *J. Environ. Qual.* **1999**, *28*, 1864−1870.
(46) Kim, S.; Dale, B. E. Environmental aspects of ethanol derived from no-tilled corn grain: nonrenewable energy consumption and greenhouse gas emissions. *Biomass Bioenerg.* **2005**, *28*, 475−489.
(47) Henderson, S. *Assessment of Net Emissions of Greenhouse Gases from Ethanol-Gasoline Blends in Southern Ontario*; Agriculture and Agri-Food Canada: 2000.
(48) Kim, S.; Dale, B. E. Cumulative energy and global warming impact from the production of biomass for biobased products. *J. Ind. Ecol.* **2004**, *7*, 147−162.
(49) West, T. O.; Marland, G. Net carbon flux from agriculture: Carbon emissions, carbon sequestration, crop yield, and land-use change. *Biogeochemistry* **2003**, *63*, 73−83.
(50) Lee, K. Comparison of fermentative capacities of lactobacilli in single and mixed culture in industrial media. *Process Biochem. (Oxford)* **2005**, *40*, 1559−1564.
(51) Gruber, P. R.; Drumright, R. E.; Henton, D. E. Polylactic Acid Technology. *Adv. Mater* **2000**, *12*, 1841−1846.
(52) Carlson, P. R.; Peters, E. M., Jr. Low Ph lactic acid fermentation. U.S. Patent 6,475,759, 2002.

*Received for review March 15, 2006. Revised manuscript received October 13, 2006. Accepted November 2, 2006.*

ES0606125