The Development and Evaluation of Biofuel Production Systems on Marginal Land

by

Xi Zhao

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Graduate Supervisory Committee:

Amy Landis, Chair
Peter Fox
Mikhail Chester

ARIZONA STATE UNIVERSITY

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ABSTRACT

The consumption of feedstocks from agriculture and forestry by current biofuel production has raised concerns about food security and land availability. In the meantime, intensive human activities have created a large amount of marginal lands that require management. This study investigated the viability of aligning land management with biofuel production on marginal lands. Biofuel crop production on two types of marginal lands, namely urban vacant lots and abandoned mine lands (AMLs), were assessed.

The investigation of biofuel production on urban marginal land was carried out in Pittsburgh between 2008 and 2011, using the sunflower gardens developed by a Pittsburgh non-profit as an example. Results showed that the crops from urban marginal lands were safe for biofuel. The crop yield was 20% of that on agricultural land while the low input agriculture was used in crop cultivation. The energy balance analysis demonstrated that the sunflower gardens could produce a net energy return even at the current low yield.

Biofuel production on AML was assessed from experiments conducted in a greenhouse for sunflower, soybean, corn, canola and camelina. The research successfully created an industrial symbiosis by using bauxite as soil amendment to enable plant growth on very acidic mine refuse. Phytoremediation and soil amendments were found to be able to effectively reduce contamination in the AML and its runoff.

Results from this research supported that biofuel production on marginal lands could be a unique and feasible option for cultivating biofuel feedstocks.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF ABBREVIATIONS

Abbreviation	Name
AAS	Atomic Absorption Spectrometer
AMD	Acid Mine Drainage
AML	Abandoned Mine Lands
ASTM	American Society for Testing and Materials
CRP	Conservation Reserve Program
EPA	Environmental Protection Agency
EISA	Energy Independence and Security Act
GHG	Greenhouse Gas
GTECH	Growth Through Energy and Community Health
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
LCA	Life Cycle Assessment
MA	90% w/w Mine Refuse and 10% w/w Bauxite Residues
MSCC	Maximum Soil Contaminant Concentrations
NEV	Net Energy Value
RFS2	Renewable Fuel Standard 2
USDA	U.S. Department of Agriculture

CHAPTER 1 – INTRODUCTION AND BACKGROUND

1.1 Motivation

Biofuel production has been rising as a major component of our sustainable energy future. The United States Renewable Fuel Standard 2 (RFS2) mandates the production of 36 billion gallons (136 billion L) of biomass-based fuel by 2022 [1, 2]. However, traditional biofuel production methods consume feedstocks mainly from agricultural and forestry sectors, and thus have raised concerns about food security and land use rights [3]. The conflicts between biofuel production and other important land uses have led to a desire to develop new biofuel production approaches that minimize the use of prime farmland [4]. Biofuel production on marginal land draws immediate research attentions as an option to resolve the land use issue for mass biofuel production. Most current research regarding marginal land biofuel focuses on marginal agricultural land and shows net environmental benefits from biofuel production on this type of land [5-9]. This thesis will extend the research to a broader range of marginal lands other than marginal agricultural land. A large amount of urban vacant lots and abandoned mine lands (AML) exist in the US as a result of the century-long industrial and urban development. Poor quality and soil contamination marginalize these lands and prevent them from being used for more common purposes. Traditional land management methods, such as vegetation, require high cost and do not return any useful products. This thesis will investigate the viability of aligning land management with beneficial land use through biofuel crop production.

Life cycle assessment (LCA) is one tool that can quantitatively evaluate the environmental sustainability of a process or product. This method tracks all emissions and materials consumptions from raw material extraction to waste disposal and convert the emissions and consumptions to comprehensible the environmental impacts [10]. LCA is one of the few methodologies for the evaluation of the environmental burdens associated with biofuel production, by identifying energy and materials used as well as waste and emissions released to the environment [11-13]. Ultimately, this thesis aims to evaluate the environmental implications of combining marginal land management with biofuel production from a life cycle perspective.

1.2 Land Use Issues Related to Biofuel Production

The pressure to reduce atmospheric emissions of CO2 to mitigate the problem of global climate changes and the concern for energy security has pushed the legal obligation of promoting biofuels in the national energy mix [14]. The United States Renewable Fuel Standard Program 2 (RFS2) that is developed based on the 2007 Energy Independence and Security Act (EISA) requires 36 billion gallons of renewable transportation fuel being produced per year by 2022 [1]. The rapidly expanding biofuel demand has caused an increasing amount of arable land being invested to biofuel production. This represents a shift in land use away from food production and poses a global dilemma, namely the need to feed humanity versus the greater monetary returns to farmers through the incorporation of lands for agro-energy [14]. The Central East region that U.S. Department of Agriculture (USDA) estimates will be able to produce 8.6 billion gallons of advanced biofuel required by the RFS2 can be viewed as an example [15]. This region is identified as one of the regions that have the most potential for near and long term development of biofuels by USDA based on feedstock and land, infrastructure, and demand [15]. It has 241 million base acres of cropland and cropland pasture plus 109.8 million acres of timberland. About 9.1 billion gallons of biofuel could be produced from 10.8 million acres of dedicated bioenergy crops plus 2.0 million acres of harvested logging residue in a year [15]. The incremental biofuel production might take up 4.5% of the available cropland and cropland pasture in the entire Central East region. In 2011, about 40% of the US corn crop was used for ethanol providing an equivalent of 7% of gasoline consumption in the country [16]. A production of 35 billion gallons of ethanol will need the entire 2011 US corn crop being devoted to biofuel production [16]. The results from previous research demonstrated that land use is the concern that must be addressed before biofuel can move forward as a renewable alternative to fossil fuels.

1.3 Biofuel Production Using Marginal Land

EISA limits not only the types of feedstocks that can be used to make renewable fuel, but also the land that these renewable fuel feedstocks may come from. Specifically excluded under the EISA definition are virgin agricultural land cleared or cultivated after December 19, 2007, as well as tree crops, tree residues, and other biomass materials obtained from federal lands [16]. Existing agricultural land includes three land categories – cropland, pastureland, and Conservation Reserve Program (CRP) land [16]. Fallow land is defined as idled cropland and is therefore included within the definition of agricultural land.

Previous research that investigated the use of CRP and fallow land as agricultural marginal land for biofuel production demonstrated net environmental benefits. These studies showed greenhouse gas (GHG) emissions reduction and positive net energy value can be produced without causing prohibitive environmental impacts such as eutrophication and habitat destruction [7-9, 17, 18]. However, the use of other types of marginal land for biofuel production has been much less investigated. RFS2 does not include marginal lands other than conserved or abandoned agricultural land for biofuel production, because the environmental impacts of agricultural activities on these lands are unclear. Some concerns regarding the use of these marginal lands include decreasing soil fertility, increasing erosion, disappearing biodiversity, and long distance between feedstock supply and demand [16]. These concerns have to be addressed before a wide range of marginal land can be used for biofuel.

1.4 Vacant Lots in Cities

U.S. cities have an average of 15% vacant, or marginal lands, which produce little to no value and are often considered blights within communities [2, 19, 20]. Without any intervention, these vacant and abandoned properties contribute to urban blight and generate municipal expenses [2]. The management of vacant lands cost city agencies hundreds of thousands of dollars annually, and this covers only basic maintenance activities such as clearing brush and debris, mowing grass and removing snow in the winter [21, 22]. The efforts to turn vacant lands into development opportunities are limited by the fact that most urban vacant lots have poor soil quality and are concentrated in high crime areas or areas having limited infrastructure access. Previous research that proposed urban gardens as an effective method for vacant lot management has demonstrated that vegetation on these vacant lands can suppress urban crime, benefit urban ecosystems and increase the value of the land [23-26]. In tandem with the proposition of converting vacant land into urban gardens is urban agriculture that has been proved to be able to generate useful products for sustainable cities [27].

Agriculture on urban land for biofuel feedstock has been suggested by an early study as a means to reduce net GHG emissions and avoid competition with food production [7]. A study about Pittsburgh demonstrated that 9,000 acres of vacant lots are available in this post-industrial city for energy crop cultivation [2], and an investigation of 31 large cities in the United States showed at least 113,000 acres of vacant lots [19]. If biofuel production is implemented on vacant lots in many U.S. cities, the feedstock output can contribute to the RFS2 [2].

Urban vacant lots can be either brownfield or grayfield. Brownfield means land whose use may be complicated by the presence or potential presence of a hazardous substance, pollutant, or contaminant [28]. A brownfield site is often associated with industrial uses. Heavy metal contamination by cadmium (Cd), zinc (Zn), chromium (Cr), nickel (Ni), lead (Pb) and arsenic (As) are possible in brownfield soils [29, 30]. Grayfield is considered as land that is economically underused [31]. A grayfield site can be left behind after non-industrial uses. Grayfield sites may include high levels of zinc (Zn), lead (Pb), and arsenic (As) [32-34].

1.5 Abandoned Mine Lands

Mining destroys vegetation, causes extensive soil damage, and alters microbial communities [35]. AML is left behind after mining activities are removed from land. AML poses many environmental risks while high heavy metal levels and instable soils are the foremost ones. Reclamation of abandoned mine land is the process to restore the ecological integrity of these disturbed areas. Re-vegetation is the most widely accepted and useful way to reduce erosion, protect soils against degradation, control pollution, improve landscape and remove threats from human beings [35, 36]. However, high soil acidity, low soil fertility and heavy metal contamination are obstacles for the success of re-vegetation. The traditional way of neutralizing the acidic mine soils is to re-spread them at the site while applying limestone (CaCO3) [37]. Various natural amendments such as saw dust, wood residues, sewage sludge, and animal manures can increase soil fertility [35]. These amendments stimulate the microbial activity and provide nutrients (N and P) and organic carbon to the soil. Desirable plants for re-vegetation on AML should be easy to establish, drought-resistant and fast growing. They should also have dense canopies and root systems, and be able to grow on nutrient deficient soil with elevated metal content [35]. Grasses, legumes and suitable native species are most commonly chosen for re-vegetation on AML [35].

Heavy metals in the AML soil and acid mine drainage (AMD) causes environmental pollution that affects many countries having historic or current mining industries [38]. AMD can contaminate the entire watershed containing the AML, and the flow of water can result in contamination in a greater area [39]. Even though AMLs are different at different locations as the type of mine varies, aluminum (Al), iron (Fe), lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), selenium (Se) and nickel (Ni) are common contaminants found in AMLs and AMD [39-41]. Heavy metal contaminants can dissolve into runoff more easily at low pH as metal hydroxides formed at neutral and alkaline environment are generally insoluble [42]. The hydroxides of Al, Fe, Pb, Cr, Zn, Cd, Cu and Ni are all insoluble.

1.6 Phytoremediation potential of Biofuel Crops

The metal contaminants most commonly found at contaminated sites are Al, Fe, Zn, Ni, Pb, As, Cd, Cr and Se [40, 41]. Unlike organic contaminants, which are oxidized to carbon oxide by microbial action, most metals do not undergo microbial or chemical degradation [40]. Their total concentration in soils persists for a long time after their introduction [40]. Environmental restoration of metal contaminated soils by traditional physical and chemical methods demands large investment of economic and technological resources [43]. Phytoremediation as a low-cost technology that uses plants to remove contaminants from the environment has become a subject of intense public and scientific interest [44]. The phytoremediation capability of some biofuel crops has been demonstrated by some previous research. Table 1 summarizes the results from these studies.

Table 1. Summary of Phytoremediation Capabilities of Biofuel Crops

Biofuel Crop	**Metal Removed**	**Main Phytoremediation Plant Part**	**Oil Source**	**Type of Biofuel**
Sunflower [45-48]	Pb, Zn, Cd, Cr	Roots, leaves & stems	Seeds	Biodiesel
Soybean [47, 49]	Cr(VI), Cr(III), Ni, Zn	Leaves & stems	Seeds	Biodiesel
Canola [50-52]	Se, As	Leaves, stems & roots	Seeds	Biodiesel
Corn [53]	Pb, Zn	Roots & leaves	Corn grains/ corn stover	Bioethanol
Switchgrass [54]	Cr	Roots	Whole plant	Bioethanol
Sorghum [55, 56]	Pb, Zn, Cd, Cu	Leaves & stems	Grain/sugar/stem	Bioethanol

CHAPTER 2 – THE VIABILITY OF BIOFUEL PRODUCTION ON URBAN MARGINAL LAND

2.1 Introduction

Like the City of Pittsburgh, many urban areas have a substantial amount of vacant or blighted lands that present both opportunities and problems. Recent data sources indicate that over 14,000 vacant lots exist throughout Pittsburgh, which accounts for more than 10% of the municipalities' land [2, 19, 57, 58]. Pittsburgh's public agencies collectively spend hundreds of thousands of dollars annually to maintain vacant lots in the city, and this covers only basic maintenance activities such as clearing brush and debris, mowing grass, and removing snow in the winter [21, 22]. Previous research has shown that plant growth on urban vacant lots can increase the resilience of urban ecosystems, suppress crime, and raise the price of the land [24-26]. Furthermore, a recent study demonstrated that wide use of the vacant lots in cities for biofuel crop production may contribute to the target set by the United States Renewable Fuel Standard 2 that requires one billion gallons biodiesel being produced per year by 2020 [2]. Large-scale biofuel production has caused wide social concerns about food security and land use rights due to its consumption of feedstocks that come largely from agriculture and forestry [3, 59, 60]. Aligning biofuel production with urban vacant lot management will not only reduce government expenditure on land management and improve urban landscape but also mitigate the land use concerns regarding biofuel production.

Most urban vacant lots have poor soil quality and are concentrated in high crime areas or areas having limited infrastructure access. They are classified as marginal lands, a term that is used to define lands that have poor agriculture potential and are unsuited for housing and other uses [61]. Previous research has shown that marginal agricultural land can be used to grow biofuel crops with net environmental benefits [6-9], but few studies investigated the use of marginal *urban* land for biofuel production. This article investigated the viability of growing biofuel crops as a way to reclaim the marginal urban land while providing feedstocks for biofuel production.

There are two concerns associated with crop cultivation on marginal urban land. First, the land may be subject to a risk of contamination as a result of various human activities that used to take place on the land or nearby. Second, crop cultivation requires energy for harvesting and transportation; there may be more energy consumed for transportation per unit output because urban sites vary in size and are fragmented across different locations. This article quantifies the degree of contamination on urban marginal land, the contaminant uptake by plants, as well as the net energy value (NEV) of biofuel production.

Existing studies have shown that contaminants in soil can enter biofuel crops such as sunflower, switchgrass, soybean, corn and canola. [43, 46, 47, 49, 52, 53, 62-64]. In this study, we examined the level of contamination in urban marginal soils by analyzing soil samples collected between 2008 and 2011 from two representative plots of marginal land in Pittsburgh. Further analysis with respect to contaminant concentrations in different parts of the plant was done to reveal whether there is a risk that the contaminants will enter the biofuel product if sunflower grown on urban marginal land is used as biofuel feedstock. Nine metals including Al, Fe, Zn, Ni, Pb, As, Cd, Cr and Se were considered to be the most likely contaminants present in Pittsburgh lots due to the city’s industrial past and large volume of human activities at present [32-34].

This study used the sunflower biofuel system developed by GTECH Strategies on Pittsburgh’s marginal land as an example of the urban marginal land biofuel system. GTECH Strategies, where GTECH stands for “Growth Through Energy and Community Health”, is a non-profit organization in Pittsburgh committed to transforming vacant or blighted properties into community economic development opportunities [65]. Sunflower was selected as the appropriate energy crop, because it has lower fertilizer requirement than other biofuel crops, is able to adapt to a broad range of soil qualities, and contributes to urban aesthetics [66]. In GTECH’s “Urban Land Use” project, the vacant lots in the city were converted to sunflower gardens and the sunflower seeds produced from these lands were used as biofuel feedstocks. NEV calculations were performed for two such sunflower gardens to determine the net energy value of producing biodiesel on urban marginal land.

2.2. Materials and Methods

2.2.1 Experimental plots

Two plots where GTECH grew sunflowers were investigated in this study. Figures 1(a) and (b) classified the major land uses and soil types around the sites based on the criteria established in a recent study about urban merginal land [2, 19, 57, 58]. The two experimental plots were in industrial and residential areas respectively. The first plot, designated as the ‘0.8 ha-Industrial Plot’, had an area of 0.8 ha and was where a steel mill previously existed. The second plot, designated as the ‘0.12 ha-Residential Plot’, had an area of 0.12 ha and was within a residential community. The pH of the 0.8 ha-Industrial

Plot and 0.12 ha-Residential Plot was 7.6 and 8.4, while the soil organic carbon content measured by the dry combustion method was 1.3% and 2% respectively [67]. These two plots had most different histories and surroundings among the 27 GTECH sunflower gardens at the time of this study. They were supposed to be a generic representation of urban vacant lots that had been subject to either industrial or residential uses but had never experienced direct contact with contaminated materials.

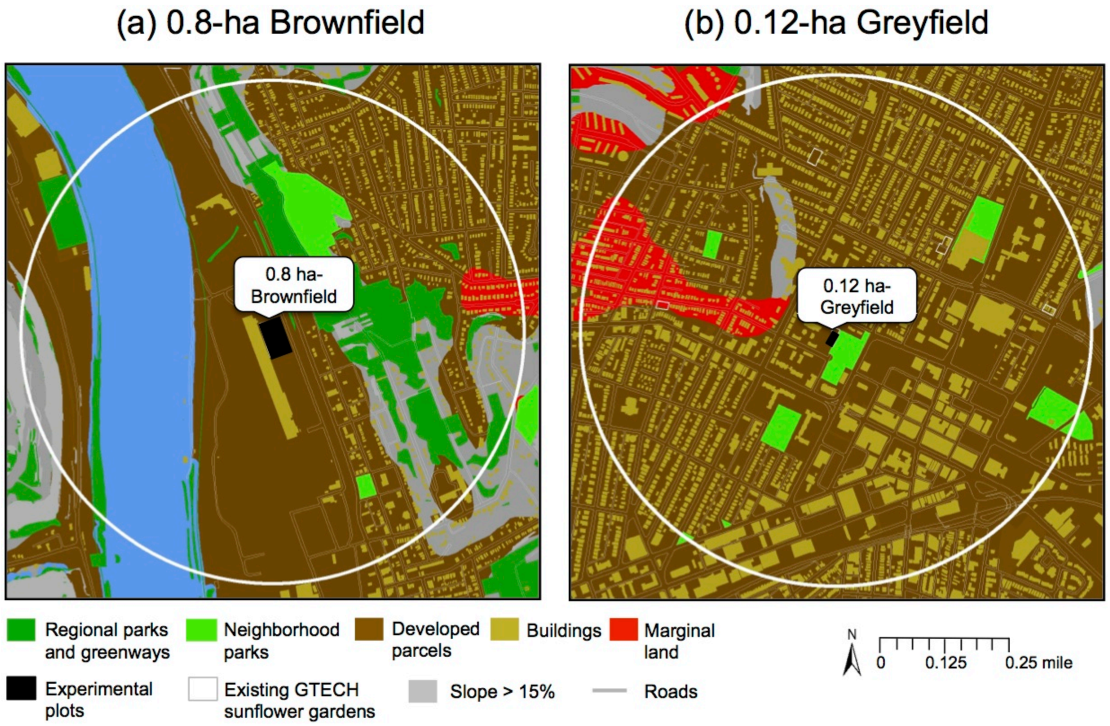


Figure 1. Experimental plot locations and major land uses around the sites

2.2.2 Crop cultivation method

GTECH employed a low input agriculture strategy to cultivate crops on the urban marginal land in order to reduce the use of chemicals and water, and minimize the cost. All of the work from field preparation to crop harvesting was done by hand with the exception that a mowing machine was used to cut weeds before planting and a walk-behind tiller was used to till the soil to a depth of 20 cm. No pesticides and irrigation were applied to the field throughout the growth of the crops. Either compost fertilizers or horse manure could be added to the field prior to the first growth cycle, if and only if the soil organic matter in a particular site was found below 3.5% w/w. No other fertilizer was used. All sunflower seeds were separated on site manually after harvesting and the heads were left on site to be chipped and re-incorporated into the soil. Cultivation using the low input method proved to be viable on marginal land in Pittsburgh, as GTECH had successfully established 27 existing sunflower gardens with a reduced seed yield of 280 kg/ha.

2.2.3 Analysis of heavy metals in soil and plant

Concentrations of Al, Fe, Zn, Ni, Pb, As, Cd, Cr and Se in the soil of the 0.8 ha-Industrial Plot and 0.12 ha-Residential Plot were monitored from 2008 summer to 2011 summer. In addition to these metals, Hg had been tested by GTECH as a prequalification for the sites to be considered for sunflower cultivation and our initial tests further proved Hg could not be detected in the experimental plots.

Soil samples were collected during this period before planting and after harvesting. On each of the plots, seven locations that were evenly distributed throughout the plot were selected for soil sampling. A total of 14 soil samples were taken from each plot, consisting of two soil samples from each sampling location at depths of 0 to 15 cm and 15 to 30cm. A coring device was used to collect soil samples whenever possible. At locations where mixed materials that could not be broken by the coring device were present, hand shovel and scoop were used for sampling. All soil samples were dried in separate crucibles in a laboratory oven at 70 °C for 24 hours before being ground by mortar and pestle. The soils samples were then sieved to 177 µm (80 mesh). We followed EPA Method 3051A to digest the soil samples [68]. In brief, 0.5 g of each of the soil samples was mixed with a digestive solution consisting of 5 mL 65% HNO_3, 2 mL 35% HCl and 43 mL deionized water and was digested in a CEM Model 5 Microwave Digestion System at 1200 W for 20 minutes at 170 °C. This method was intended to dissolve all elements that could become environmentally available and achieved 45-70% digestion of the soil samples with respect to the total dry mass in our analysis [68]. The sample extracts were subsequently passed through 450 nm Millipore mixed cellulose ester filters before being analyzed by Atomic Absorption Spectrometer (AAS). The concentrations of Al, Fe, Zn, Ni and Pb were analyzed by a Perkin Elmer 1100B flame AAS and the concentrations of As, Cd, Cr and Se were analyzed by a Perkin Elmer 4100ZL graphite furnace AAS. Appropriate dilutions were made when the sample concentration of a particular metal exceeded the detection limit of the instrument. Metal concentrations in the soil were obtained by dividing the mass of the metal in the extract by the mass of the soil extracted.

Quality control measures were taken for soil analysis. Control samples were taken from a predetermined undisturbed location in the plot each time soil samples were collected in order to verify the consistency of the results of analysis of samples obtained at different times. The soil samples were transported and kept in sealable polyethylene food storage bags for no more than 5 days before digestion. The soil extract solutions were kept in high-density polyethylene sample bottles cleaned by 3% HNO_3 and deioninzed water prior to AAS analysis. No labware made of the metals being analyzed was used in contact with the samples. Reagent blank consisting of the same acids went through the whole digestion process with the samples. The absence of contamination from sample digestion was verified as no reagent blank had metal concentrations that were detectable by the instrument used for the analysis. All AAS analyses were done in three replicates. The results were recorded only when the difference between replicate measurements were smaller than 5%. The average of the three measurements was regarded as the sample concentration. The instrument was rechecked with the standards every 15-20 sample analyses to ensure accuracy.

Entire sunflower plants were collected from both the 0.8 ha-Industrial Plot and 0.12 ha-Residential Plot at the end of the growth seasons for the analysis of the metal contaminants in plants. The sunflowers were first washed with tap water to remove any soil attached to them and then air dried for 3 weeks. The dry plants were separated into root, stalk, leaf and flower head before being chopped by a household blender. Subsequently, 0.5 g of each of the four parts of the plants was digested by the same method as the soil analysis. The concentrations of the same nine metals were analyzed for the plant samples by the same method used in the soil analysis. The quality control for plant digestion and metal determination followed similar measures as in the soil analysis.

2.2.4 Soil metal concentration data analysis

Student's t-test was employed to assess the differences in mean soil metal concentrations in one plot at different times with the assumption that the concentration followed normal distribution [69]. A t-test sample used consisted of all soil samples collected at one plot at one time. Paired t-test was performed, since the t-test samples being compared were paired samples from one same plot on different dates. The details of the t-test are given in Table 2. The null hypothesis would be rejected if the P-value was less than 0.05, indicating that the soil metal concentration had either increased or decreased.

Table 2. Student's t-test on the difference in soil metal concentration means

	Details of the Test	Description of Notation
Null hypothesis	H_0: $\mu_1 - \mu_2 = 0$	μ_1: mean concentration at time 1 μ_2: mean concentration at time 2
Alternative hypothesis	H_1: $\mu_1 - \mu_2 \neq 0$	μ_1: mean concentration at time 1 μ_2: mean concentration at time 2
Type of test	Paired two-sample t-test	
Type of P-value	Two-tailed P-value	
Level of significance	α=0.05	

2.2.5 Net energy value of the system

The NEV of GTECH sunflower biofuel system was calculated by subtracting the total energy input from the energy output. This study considered only primary energy inputs to the biodiesel production. Secondary inputs, such as the energy used to manufacture the materials used in the construction of the biofuel facilities, farm equipment, and vehicles were excluded from the NEV because they account for a negligible portion of energy consumption on a per-gallon basis after being distributed over the total production during the lifetime of the facilities [70]. The total energy input was obtained by summing up all the nonrenewable energy required to produce biodiesel from field preparation to biofuel processing and included the upstream energy consumption, such as the life-cycle energy required to produce truck fuel and electricity. Life cycle energy efficiencies for different energy sources obtained from the GREET1_2011 model were used in the energy input calculation to account for upstream energy use [71]. The energy output was calculated as the energy content in the final products. Table 3 summarizes the equations and data sources that were used to calculate the energy consumptions in different life-cycle stages and the energy output from the products. Data regarding inputs to the sunflower gardens and seed yield were based on GTECH's field records. The fuel efficiency of the vehicle used by GTECH was obtained from factory specifications. The processing capability and electricity consumption rate of the crusher was from a study using the same equipment [71]. The GREET1_2011 model published by Argonne National Laboratory that provided values representing U.S. national average levels was used as much as possible to evaluate the energy consumption in transportation fuel and biofuel processing [71]. For some parameters regarding the density and energy content of products, peer-reviewed publications that reported average values from large-scale applications were used as the data sources [71].

Table 3. Equations Used in Net Energy Value Calculation

x = life cycle stage; f = field preparation; t1 = transport during sunflower production; t2 = intra-city transport after harvest; t3 = intercity transport after harvest; e = sunflower oil extraction; c = sunflower oil to biodiesel conversion; d = biodiesel distribution

	Equation for Energy Input/output Calculation	**Parameter Description**	**Data Source**
Total Energy Input	Equation 1: $E_{in} = \sum E_x$	E_{in} = total energy input (MJ)	Calculated in this study
		E_x = energy input in individual life cycle stage (MJ)	Calculated in this study
Energy input in Individual Production Phase			
Sunflower production			
• Field preparation (mowing and tilling)	Equation 2: $E_f = F_f \times H_{gas} \times RE^{-1}$	E_f = energy input in field preparation (MJ)	Calculated in this study
		F_f = gasoline use in field preparation (L)	GTECH Strategies [67]
		H_{gas} = lower Heating Value of gasoline (MJ/L)	GREET1_2011 [71]
		RE = refining efficiency for gasoline	GREET1_2011 [71]
• Transport	Equation 3: $E_{t1} = D_{t1} \times FE^{-1} \times H_{gas} \times RE^{-1}$	E_{t1} = energy input in transport during sunflower production (MJ)	Calculated in this study

		D_{t1} = distance travelled during sunflower production (km)	Estimated according to locations of lots
		FE = vehicle fuel efficiency (km/L)	GMC Canyon 1-ton pickup technical specifications
		H_{gas} = lower Heating Value of gasoline (MJ/L)	GREET1_2011 [71]
		RE = refining efficiency for gasoline	GREET1_2011 [71]
Transport after harvest			
• Transport within Pittsburgh	Equation 4: $E_{t2} = D_{t2} \times FE^{-1} \times H_{gas} \times RE^{-1}$	E_{t2} = energy input in intra-city transport after harvest (MJ)	Calculated in this study
		D_{t2} = distance travelled within Pittsburgh after harvest (km)	Estimated according to locations of lots
		FE = vehicle fuel efficiency (km/L)	GMC Canyon 1-ton pickup technical specifications
		H_{gas} = lower Heating Value of gasoline (MJ/L)	GREET1_2011 [71]
		RE = refining efficiency for gasoline	GREET1_2011 [71]
• Intercity transport	Equation 5: $E_{t3} = D_{t3} \times FE^{-1} \times Y_{t3} \times d \times L^{-1} \times H_{gas} \times RE^{-1}$	E_{t3} = energy input in intercity transport after harvest (MJ)	Calculated in this study
		D_{t3} = distance travelled between GTECH headquarter and Pennsylvania State University	Distance calculated by Google Map
		FE = vehicle fuel efficiency (km/L)	GMC Canyon 1-ton pickup technical specifications
		Y_{t3} = amount of seeds from each plot (m^3)	GTECH Strategies [67]
		d = sunflower seeds density (kg/m^3)	Gupta, R.K. and Das, S.K. [72]
		L = vehicle load capacity (kg)	GMC Canyon 1-ton pickup technical specifications
		H_{gas} = lower Heating Value of gasoline (MJ/L)	GREET1_2011 [71]
		RE = refining efficiency for gasoline	GREET1_2011 [71]
Biofuel processing			
• Sunflower oil extraction	Equation 6: $E_e = Y_e \times d \times P^{-1} \times EU \times EE^{-1}$	$E_{i,x}$ = energy input in sunflower oil extraction (MJ)	Calculated in this study
		Y_e = amount of seeds processed (m^3)	GTECH Strategies [67]
		d = sunflower seeds density (kg/m^3)	Gupta, R.K. and Das, S.K. [72]
		P = processing capability of the oil expeller (kg/hr)	Backer, L. et al. [73]
		EU = electric energy use of the crusher (MJ/hr)	Backer, L. et al. [73]
		EE = power plant energy conversion efficiency	GREET1_2011 [71]

• Sunflower oil to biodiesel conversion	Equation 7: $E_c = S_c \times C^{-1} \times EI_c$	E_c = energy input in biodiesel conversion (MJ)	Calculated in this study
		S_c = sunflower oil processed (kg)	GTECH Strategies [67]
		C_x = conversion ratio from sunflower oil to biodiesel (kg/kg)	GREET1_2011 [71]
		EI_c = Energy use intensity in biodiesel conversion (MJ/kg)	GREET1_2011 [71]
Biofuel distribution	Equation 8: $E_d = O_d \times EI_d$	E_d = energy input in biodiesel distribution (MJ)	Calculated in this study
		O_d = biodiesel distributed (kg)	Calculated based on sunflower oil yield from GTECH Strategies
		EI_d = energy use intensity in biodiesel distribution (MJ/kg)	GREET1_2011 [71]
Energy Output from Products			
• Biodiesel	Equation 9: $E_{biodiesel} = S_{oil} \times C_{biodiesel}^{-1} \times H_{biodiesel}$	$E_{biodiesel}$ = energy output from biodiesel (MJ)	Calculated in this study
		S_{oil} = sunflower oil produced from each plot (kg)	GTECH Strategies [67]
		$C_{biodiesel}$ = ratio from sunflower oil to biodiesel (kg/kg)	GREET1_2011 [71]
		$H_{biodiesel}$ = lower heating value of sunflower biodiesel (MJ/kg)	Mehta, P.S. and Anand, K. [74]
• Sunflower meal	Equation 10: $E_{meal} = S_{oil} \times R \times M$	E_{meal} = energy output from sunflower meal (MJ)	Calculated in this study
		S_{oil} = sunflower oil produced from each plot (kg)	GTECH Strategies [67]
		R = ratio between sunflower meal and sunflower oil (kg/kg)	Kallivroussis, L. et al. [75]
		M = metabolizable energy content in sunflower meal (MJ/kg)	Kallivroussis, L. et al. and Rossell, J.B. et al. [75, 76]
• Glycerin	Equation 11: $E_{glycerin} = S_{oil} \times C_{glycerin}^{-1} \times H_{glycerin}$	$E_{glycerin}$ = energy output from glycerin (MJ)	Calculated in this study
		S_{oil} = sunflower oil produced from each plot (kg)	GTECH Strategies [67]
		$C_{glycerin}$ = ratio between sunflower oil and glycerin (kg/kg)	GREET1_2011 [71]
		$H_{glycerin}$ = Energy content of glycerin (MJ/kg)	GREET1_2011 [71]

The crop cultivation and harvesting stages did not appear in the calculation because they did not consume energy from nonrenewable sources under GTECH's low input agriculture; rather, community members and other volunteers harvested the crops by hand. No machines driven by fossil fuels or synthetic fertilizers were used during crop cultivation and harvesting. The energy to transport workers was also assumed to be negligible since GTECH engaged volunteers who lived nearby the plots and walked to the plots.

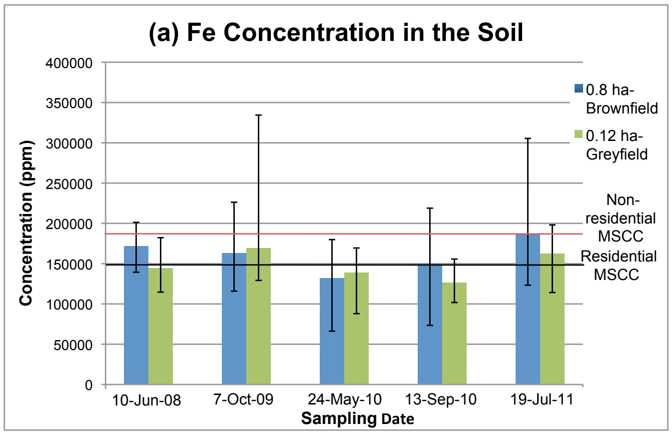
The GTECH process involved both local and intercity transport. Local transport between GTECH and the plots was done twice in each growth cycle. The first visit was to prepare the land and plant the crop while the second visit was done after harvest to move the seeds from the plot to GTECH headquarter to be air-dried and collected with seeds from other plots. The average distance between GTECH and its plots was estimated to be six kilometers. All seeds were subsequently transported 218 kilometers from Pittsburgh to the Pennsylvania State University to be crushed. The sunflower oil was eventually sent back to a Pittsburgh's biofuel plant to be converted into biodiesel.

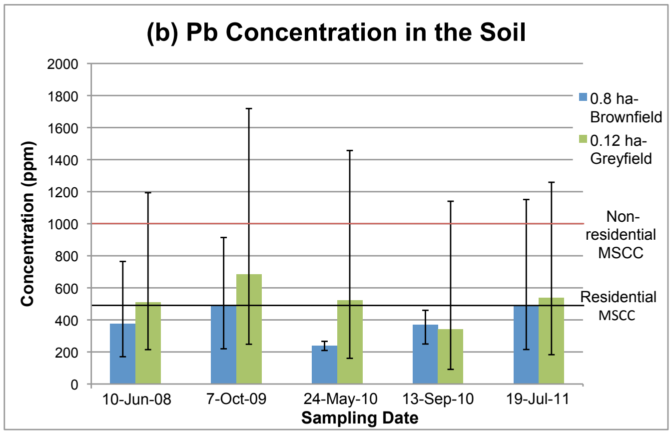
The equations in Table 3 were used to calculate the NEV of the urban sunflower biofuel system based on data from the two GTECH sunflower gardens. The NEV varied with different sunflower gardens as the parameters in the equations changed. In order to quantify how significantly the NEV could be impacted by change in factors like plot size, seed yield, energy input allocated to by-products and transport amount, a sensitivity analysis was carried out with respect to each of these parameters. The sensitivity analysis tested the input parameters through either increasing or decreasing the value of one parameter by 50% while holding the other parameters in the equations the same as the original data from GTECH. A change of 50% was arbitrarily selected for the analysis, because the value of plot size, seed yield, energy input allocated to by-products and transport amount was able to vary freely over a wide range. The NEV obtained after changing one of the parameters was eventually compared to the original NEV to reveal how a particular factor can influence the results under certain circumstances.

2.3 Results and Discussion

2.3.1 Heavy metals in marginal soils

Amongst the nine metals analyzed for soil samples, only Fe, Pb and As were observed to exceed the residential maximum soil contaminant concentrations (MSCCs) issued by the Pennsylvania Department of Environmental Protection [77]. The concentrations of all other metals ranged from 1% to 50% of the MSCCs. (The complete soil metal concentration results are available in Table A and B in the Appendix.) Figure 2 shows the average concentrations as well as the maximum and minimum concentrations of Fe, Pb and As monitored between 2008 and 2011 in comparison with the residential MSCCs and non-residential MSCCs. Other than the Pb concentrations observed on October 7, 2009 and May 24, 2010, the difference between the average concentrations in the 0.8 ha-Industrial Plot and 0.12 ha-Residential Plot, was within 20%. Based on the metal concentrations detected on both Industrial Plot and Residential Plot, the marginal land in Pittsburgh is subject to a risk of contamination by Fe, Pb and As to a level that prevents residential use.





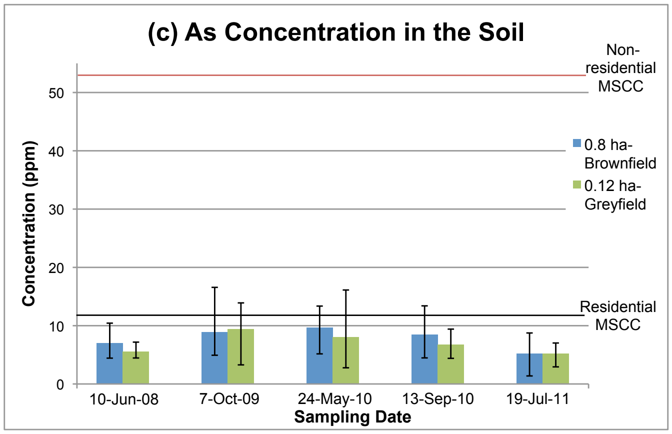


Figure 2. Average concentrations of Fe, Pb and As in soil compared with maximum soil contaminant concentrations (MSCCs) (error bars represent maximum and minimum concentrations observed in each plot)

Figure 3 shows the change of the average concentrations of metals in the 0.8 ha-Industrial Plot and 0.12 ha-Residential Plot on a normalized basis with respect to the crops grown in between the sampling dates. The concentrations of all metals, except As in the 0.12 ha-Residential Plot, oscillated within a range of 50% from their original values in 2008 summer throughout the period of investigation.

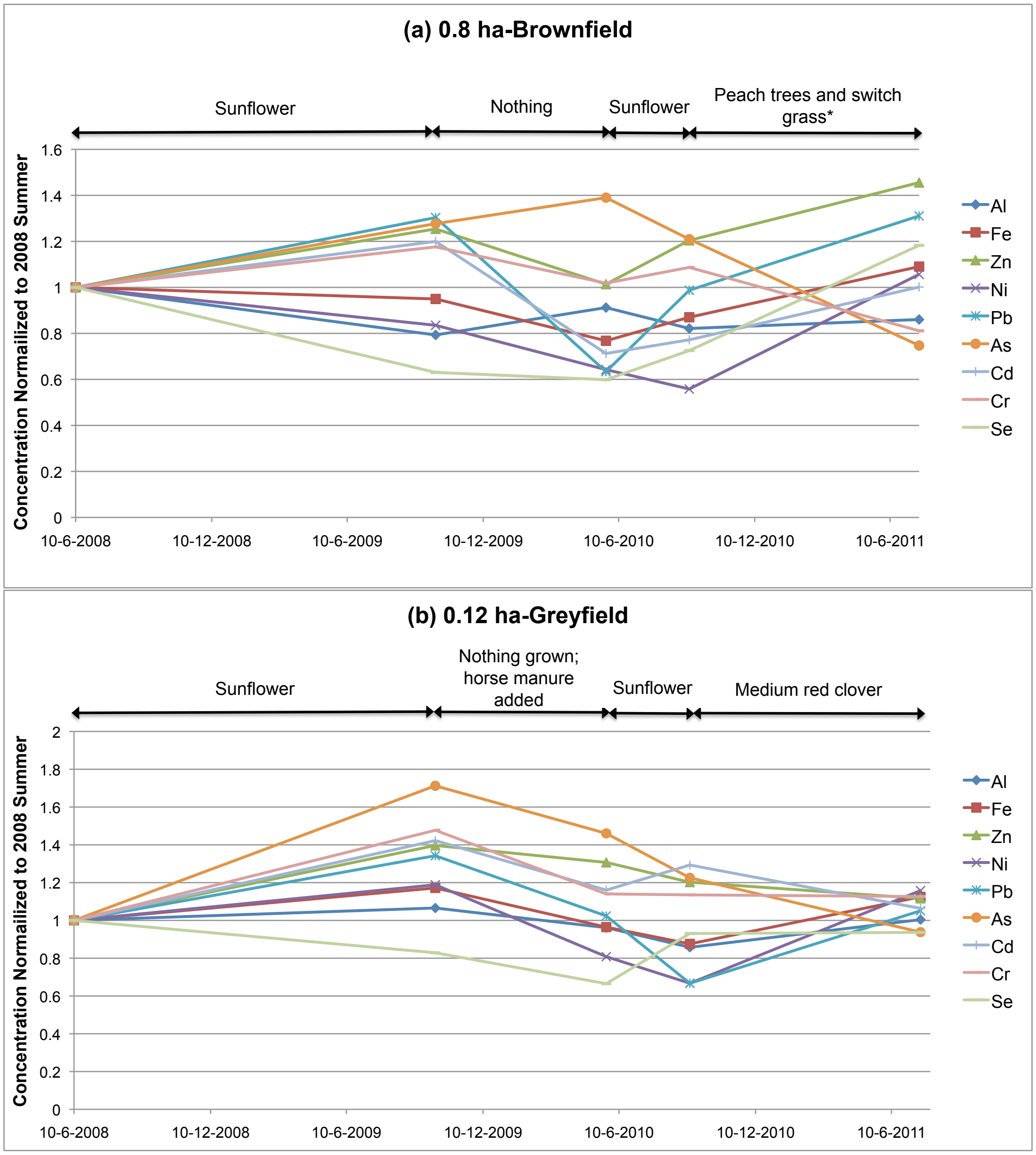


Figure 3. Average soil metal concentrations from 2008 to 2011 normalized to 2008
* The switch grass was not intentionally grown as a crop on the field. It grew on the 0.8 ha-Industrial Plot, because it had been planted on site prior to 2008.

The Student's t-test was employed to determine whether the null hypothesis, $H_{0:}$

the average soil metal concentrations at two sampling dates were equal, was true. Table 4 summarizes the results of the t-test. While fluctuation in soil contaminant concentrations was observed for some metals between some sampling dates, the metal levels were more likely to remain unchanged as more than 80% of the test results indicated no change in concentration (Table 4). The concentration of all the metals, except Al and As in the 0.8 ha-Industrial Plot, could be considered as unchanged between 2008 and 2011. These results demonstrated that metal contaminant levels in GTECH sunflower gardens were consistent in the study period.

Table 4. Results of Hypothesis Testing for the Change of Metal Concentrations

0.8 ha-Industrial Plot		Jun. 10, 2008 – Oct. 7, 2009	Oct. 7, 2009 – May 24, 2010	May 24, 2010 – Sep. 13, 2010	Sep. 13, 2010 – Jul. 19, 2011	Jun. 10, 2008 – Jul. 19, 2011
Crops Grown on the Site		Sunflower	No crops cultivated	Sunflower	Peach trees and switch grass	
Results of Statistical Analysis of Concentration Change	Al	Decrease	No change	No change	No change	Decrease
	Fe	No change	No change	No change	No change	No change
	Zn	Increase	No change	No change	No change	No change
	Ni	No change	No change	No change	Increase	No change
	Pb	No change	No change	No change	No change	No change
	As	No change	No change	No change	Decrease	Decrease
	Cd	No change	No change	No change	No change	No change
	Cr	No change	No change	No change	Decrease	No change
	Se	No change	No change	No change	Increase	No change

0.12 ha-Residential Plot		Jun. 10, 2008 – Oct. 7, 2009	Oct. 7, 2009 – May 24, 2010	May 24, 2010 – Sep. 13, 2010	Sep. 13, 2010 – Jul. 19, 2011	Jun. 10, 2008 – Jul. 19, 2011
Crops Grown on the Site		Sunflower	No crops cultivated	Sunflower	Medium red clover	
Soil Amendment Applied to the Site		None	Horse manure	None	None	
Results of Statistical Analysis of Concentration Change	Al	No change	No change	No change	No change	No change
	Fe	No change	No change	No change	Increase	No change
	Zn	Increase	No change	No change	No change	No change
	Ni	No change	Decrease	No change	Increase	No change
	Pb	No change	No change	No change	Increase	No change
	As	Increase	No change	No change	Decrease	No change
	Cd	No change	No change	No change	No change	No change
	Cr	Increase	Decrease	No change	No change	No change
	Se	No change	No change	No change	No change	No change

2.3.2 Heavy metals in plants

Results from this study showed limited metal uptake by sunflowers on urban marginal land and indicated them as safe feedstocks for biodiesel. Metal content in the root, stalk, leaf, and head of the sunflowers from the 0.8 ha-Industrial Plot and 0.12 ha-Residential Plot are summarized in Table 5. The concentrations of all metals in the stem, leaf and head parts of the plant samples were no more than 1% of the concentrations in the soil except that the concentrations of Zn and Cd in these parts were 5-10% of the soil concentrations. Metal concentrations in the root were higher than the top parts, but did not exceed 10% of that of the soil concentrations. No metal concentration in the urban marginal land sunflowers was higher than that reported by previous studies for sunflowers grown on regular soil, except for Fe whose concentration in the parts of urban marginal land sunflowers was 3-5 times that of sunflowers from regular soil (Madejón et al., 2003, National Sunflower Association, 2004). However, Fe concentration was not regulated by the ASTM D6751 standard (ASTM International, 2008), which was acknowledged by the U.S. EPA as the measure for biodiesel quality (U.S. EPA, 2007b).

The fact that soil contamination in GTECH sites was limited to only Fe, Pb and As to a maximum of residential MSCC level contributed to the safe metal concentrations in urban marginal land sunflowers. Some studies that grew sunflowers on soils 3-10 times more contaminated by one or more metals than this study reported 2-8 fold increase in Zn, Pb, As and Cr concentrations in plant [45-48, 53, 63]. Feedstock safety needed to be reevaluated if sunflowers were cultivated on these contaminated lands.

Table 5. Metal Concentrations in Different Parts of the Sunflower Samples

		Al (ppm)	Fe (ppm)	Zn (ppm)	Ni (ppm)	Pb (ppm)	As (ppm)	Cd (ppm)	Cr (ppm)	Se (ppm)
Head	0.8 ha-Industrial Plot	249	358	17	B.D.L.	B.D.L.	B.D.L.	0.1	1.6	B.D.L.
	0.12 ha-Residential Plot	263	501	18	B.D.L.	B.D.L.	B.D.L.	0.1	1.4	B.D.L.
Leaf	0.8 ha-Industrial Plot	230	319	107	B.D.L.	B.D.L.	B.D.L.	0.1	0.7	B.D.L.

	0.12 ha-Residential Plot	235	434	92	5.4	B.D.L.	B.D.L.	1.5	0.2	B.D.L.
Stalk	0.8 ha-Industrial Plot	44	173	15	B.D.L.	B.D.L.	B.D.L.	0.1	B.D.L.	B.D.L.
	0.12 ha-Residential Plot	125	280	22	2.6	B.D.L.	B.D.L.	0.1	0.3	B.D.L.
Root	0.8 ha-Industrial Plot	3988	4649	90	B.D.L.	28	0.8	0.1	10.8	0.4
	0.12 ha-Residential Plot	3976	6774	53	5.8	25	B.D.L.	0.2	8.5	0.5

B.D.L. = Below Detection Limit

2.3.3 System energy balance

The NEV calculation for the sunflower biofuel system used GTECH's average seed yield of 280 kg/ha in Pittsburgh, and the average distance of 12 km between GTECH and its plots was assumed. The average yield and distance were used for both the experimental plots to demonstrate the differences in NEV as a result of different plot size. Table 6 shows four scenarios for calculating the energy input and output of the sunflower biofuel system on the 0.8 ha-Industrial Plot and 0.12 ha-Residential Plot. (Details of the calculation and data sources are available in the Appendix.) Both plots would generate a negative energy balance under GTECH's current process, which included a 218-km intercity transport between Pittsburgh and University Park, Pennsylvania (Table 6, Scenario 1). The intercity transport was required solely because the crusher GTECH used to get sunflower oil from the seeds was located at University Park, PA. Therefore, the energy balance of GTECH's process could be improved through the use of local biofuel production facilities. If the entire production was carried out locally, 341 MJ or 38% of the total energy input on the 0.8 ha-Industrial Plot and 51 MJ or 22% of the total energy input on the 0.12 ha-Residential Plot could be avoided. This would give rise to a net energy yield of 83 MJ on the 0.8 ha-Industrial Plot, and, a reduced energy loss of 82 MJ on the 0.12 ha-Residential Plot, if biodiesel was the only product considered (Table 6, Scenario 2).

Additional energy gains could be demonstrated by considering energy content in sunflower meal and glycerin, which are byproducts resulting from the sunflower oil extraction process and the transesterification process to make biodiesel. Data in Table 6, Scenario 3 treated these two products and the biodiesel all as the desirable products from the system. The total energy output given in Table 6, Scenario 3 is the sum of the heat energy content in biodiesel and glycerin, and the metabolic energy content in sunflower meal. The heat energy content was calculated as the product of the lower heating value and mass of products, while the metabolic energy content was the product of metabolic energy in unit mass of sunflower meal and the mass of sunflower meal. Inclusion of the energy content in all the products will increase the energy yield on the 0.8 ha-Industrial Plot to 472 MJ and reduce the energy loss on the 0.12 ha-Residential Plot to only 24 MJ.

Table 6, Scenario 4 demonstrates the energy balance when only part of the total energy investment was allocated to biodiesel production based on the market value of all products. The average prices for biodiesel, sunflower meal and glycerin were assumed to be \$1.03/kg, \$0.17/kg and \$0.33/kg respectively [71]. Market value was selected as the benchmark for the allocation because the end uses as well as the usefulness of biodiesel, sunflower meal, and glycerin are very different. Allocation by market value could better account for these differences than other allocation methods (available in the Appendix) based on energy content, mass, and energy displacement [78]. Following the market value-based allocation, the 0.8 ha-Industrial Plot gave an energy yield of 221 MJ while the 0.12 ha-Residential Plot returned an energy loss of 32 MJ.

Table 6. Energy Input and Output on the 0.8 ha-Industrial Plot and 0.12 ha-Residential Plot

Unit: MJ	Scenario 1		Scenario 2		Scenario 3		Scenario 4	
	Unallocated; intercity transport included		Unallocated; intercity transport excluded		Energy output of all products considered; intercity transport excluded		Allocated by market value of products; intercity transport excluded	
	0.8 ha-Industrial Plot	0.12 ha-Residential Plot	0.8 ha-Industrial Plot	0.12 ha-Residential Plot	0.8 ha-Industrial Plot	0.12 ha-Residential Plot	0.8 ha-Industrial Plot	0.12 ha-Residential Plot
Sunflower production								
• Field preparation	271	39	271	39	271	39	193	28
• Transport	56	56	56	56	56	56	40	40
Transport after harvest								
• Transport within Pittsburgh	56	56	56	56	56	56	40	40
• Transport to and from University Park, PA	341	51						
Biofuel processing								
• Sunflower oil extraction	77	12	77	12	77	12	55	8
• Sunflower oil to biodiesel	98	15	98	15	98	15	91	14
Biofuel distribution	5.8	0.9	5.8	0.9	5.8	0.9	5.8	0.9
Total energy input	905	230	563	179	563	179	425	129
Energy output								
• Biodiesel	646	97	646	97	646	97	646	97
• Sunflower meal					323	48		
• Glycerin					67	10		
Total energy output	646	97	646	97	1036	155	646	97
Net energy value	-259	-133	83	-82	472	-24	221	-32

Many factors could affect the net energy value on a particular plot. The reason why the 0.8 ha-Industrial Plot produced a net energy yield while the 0.12 ha-Residential Plot lost energy was that the area and hence the crop output of the 0.8 ha-Industrial Plot, was several times greater than that of the 0.12 ha-Residential Plot. The transport distance between the plots and GTECH headquarter was constant for each plot regardless of plot size and crop output. Therefore, an increasing portion of the total energy input would be spent on smaller plot with less crop output. The plot size corresponding to the energy breakeven point could be solved by setting the total energy input equal to the output in Table 3 while holding the values of other parameters unchanged. If all GTECH's production parameters and the market value allocation scheme in Table 6, Scenario 4 were used, the minimum size to avoid negative NEV on a plot could be determined as 0.2 ha. Given the seed yield of 280 kg/ha in Pittsburgh, the energy breakeven plot size of 0.2 ha indicated only plots that could produce more than 56 kg seeds had the potential for net energy production. Other than plot size, factors like seed yield on unit area, market value of by-products which influenced how much energy input could be allocated to the by-products, and amount of transport were also able to alter the net energy value of the system. Figure 4 shows how 50% fluctuation of one of these parameters while others were held constant would affect the NEVs in Table 6, Scenario 4. The NEVs obtained assuming U.S. sunflower agriculture's average yield of 1330 kg/ha could be achieved on the plots are also shown in Figure 4 [70, 79]. Cutting down the amount of transport by 50% was the most effective way to make the energy balance on the 0.12 ha-Residential Plot be positive, but it impacted the energy balance on the 0.8 ha-Industrial Plot least. This implied a quickly diminishing significance of the amount of transport on the system energy balance with increasing plot size. Apart from amount of transport, seed yield was the most influential factor determining the energy balance of both of the plots, followed by plot area and market value of by-products. A 50% increase in seed yield would be able to increase the energy balance on the 0.12 ha-Residential Plot to a positive value. If U.S. sunflower agriculture's average yield of 1330 kg/ha from could be achieved, the NEVs on the 0.8 ha-Industrial Plot and 0.12 ha-Residential Plot could be increased to more than 700 MJ and more than 35MJ respectively (Figure 4) [70, 79].

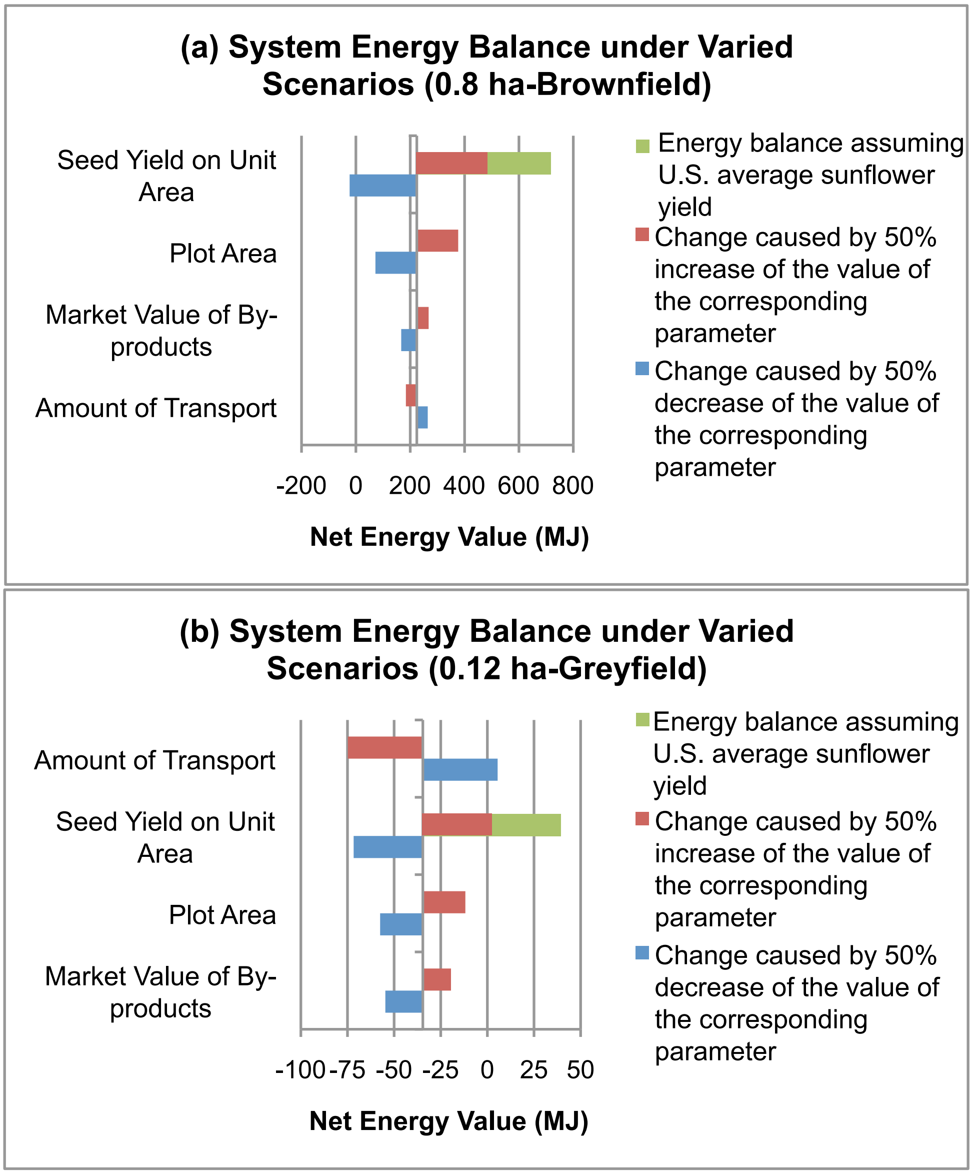


Figure 4. System energy balance resulting from changing parameters

In the GTECH system, the transportation of workers to the plots was avoided through the use of volunteers from the community. In case transportation was needed for the labor force, the total energy input could be increased by approximately 3.2 MJ per kilometer of transportation per vehicle based on an average car fuel efficiency of 10 km/L and gasoline lower heating value of 32.3 MJ/L [71]. Given that GTECH usually invited 5-15 volunteers to work on its plots, using community volunteers who were able to walk to the plots could save 32-96 MJ of energy that might be consumed if each worker drove 2 km to and from the site. These energy savings could account for a significant portion of the total energy input when compared to the values in Table 5. Hence, engaging community volunteers to work on the plots could be an important factor to increase the system NEV.

The sunflower biofuel systems on urban marginal land also created extra benefits that were not considered in the energy balance calculation. For example, the energy used in the sunflower gardens saved the energy that was originally spent to maintain these vacant lots. Moreover, each GTECH reclamation project leveraged additional resources, helping to improve environmental conditions in communities while integrating green job training as a means of transitioning problematic spaces into productive places in benefit of community [65]. Social life cycle assessment might be performed to quantify these benefits in the future.

2.4. Conclusions

In this research, the environmental implication of using urban marginal land for biofuel production was evaluated from the perspectives of soil quality, crop cultivation under urban context, and system energy balance. Three years' monitoring of metal concentrations in the experimental plots determined that heavy metal concentrations were below residential MSCC most of the time and never above industrial MSCC. Marginal land in Pittsburgh could be subject to a risk of being contaminated by Fe, Pb and As to a level that was not appropriate for residential purposes. The experimental plots were a generic representation of urban marginal land in industrial and residential areas that had no direct contamination history. The results from this study demonstrated low input agriculture was able to produce sunflowers on urban lots having similar soil quality. The metal contaminant levels in the experimental plots were consistent over time under GTECH operation. This indicated that sunflower cultivation could be a long-term practice on urban vacant lots without causing concerns about varying soil contaminant concentrations.

The little to no land contamination and low level of metal uptake by the plant tissues made sunflowers from the experimental plots in Pittsburgh a safe feedstock for biodiesel. However, this might not be true had sunflowers been grown on more contaminated soils, especially those having contaminant concentrations higher than the industrial MSCCs. In such case, the heavy metal content in the final biofuel product should be analyzed. If heavy metal removal methods are necessary in order to get safe products, the energy consumption in these steps needs to be included in the energy consumption.

The energy balance calculation in this study demonstrated that local biofuel production and adequate lot size were important to improve the NEV of the urban biofuel system. Under GTECH operation, lots in Pittsburgh with size greater than 0.2 ha were able to produce positive NEV if the biofuels were processed locally. A positive NEV would promote the possibility of coupling vacant lot management with useful biofuel crop production and avoid the costly land maintenance activities done in the past.

CHAPTER 3 – BIOFUEL CROP CULTIVATION ON ABANDONED MINE LAND

3.1 Introduction

With some two to four tons of bauxite residue arising for every ton of aluminum produced, the management of bauxite residue has always been a significant issue for the aluminum industry [80]. This study is an effort to look for sustainable bauxite residue management methods. Since bauxite residue has high pH, residueal liming capacity, and clay-like soil texture, there is an opportunity for industrial synergy that uses bauxite residue instead of lime to neutralize the acidic mine refuse for vegetative cover development. This research investigates the possibility of growing biofuel crops on acidic mine refuse using bauxite residue as soil amendment. The experiments that tests biofuel crop growth on acidic coalmine refuse mixed with bauxite residue are carried out in our greenhouse. The coalmine refuse is obtained from the Mather Mine in Greene County, Pennsylvania shown in Figure 5. The Mather Mine, which is well known for its explosion in 1928 that killed 195 miners, was closed in 1964. The contamination from the abandoned mine site poses an immediate threat to the thousands of residents in the community nearby. Runoff from the site pollutes the river that passes around it, causing greater pollution to the environment. In addition, the site suffers from other problems including erosion, subsurface fire, etc. Vegetation has proved to be effective in controlling these problems. This research aims to make the AML management practice more sustainable through cultivating useful biofuel crops on these lands.

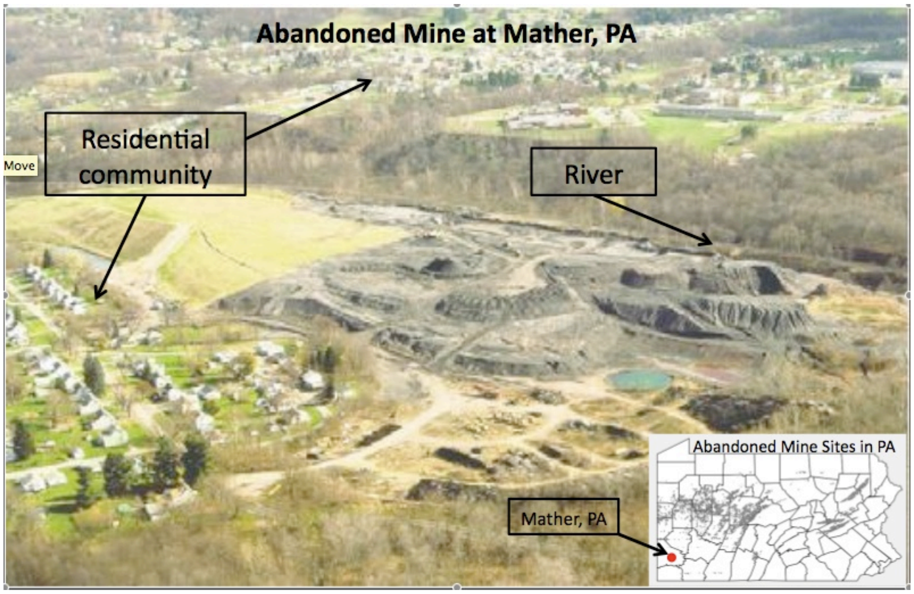


Figure 5. Abandoned mine site at Mather, PA

3.2 Approach and Methodology

3.2.1 Crop cultivation on mine refuse

Synergy between aluminum production and acidic mine refuse management is created to cultivate biofuel crops on AML. Biofuel crops were grown in greenhouse on mine refuse obtained from Mather, PA. Lime, which was added to the mine refuse to neutralize the acidity in the common re-vegetation process, was replaced by bauxite residue obtained from a local alumina refinery. Bauxite residue was mixed with mine refuse in 20-gallon nursery pots with a mass ratio of 1/9 before seeds were added to it. The soil mixture in each pot weighed 70 kg. The efficacy of bauxite residue at neutralizing mine refuse acidity is determined by soil measurements along plant growth.

The first growth cycle was completed in a greenhouse located inside of an office building at the University of Pittsburgh, as shown in Figure 6 (a). The greenhouse had an area of approximately 220 sf. Ten 432-watt fluorescent light panels provided full spectrum of light 12 hours a day for plant photosynthesis. The temperature in the office building was controlled at 20 °C at all times. Five energy crops including corn, camelina, canola, sunflower and soybean were grown in the greenhouse. All plants were irrigated with the amount of water suggested for commercial corn production, since corn has the highest water demand among the crops [81]. A total of 25 inches of water was added to each pot during the plant growth. Since Pennsylvania had an annual rainfall of about 40 inches, this represented a scenario in which the entire water needs for plant growth were provided by natural precipitation. None of the plants achieved full growth during the first growth cycle. Reasons were identified as lack of air circulation in the greenhouse and low artificial light use efficiency by plants.

The second growth cycle were carried out on the same soil in the greenhouse at Arizona State University, as shown in Figure 6 (b). Sorghum, sunflower and camelina and canola were cultivated. Corn and soybean died in the previous cultivation experiment, so they were not grown in the second experiment. The greenhouse was equipped with specifically designed ventilation system to allow the exchange of indoor and outdoor air. Constant airflow was maintained within the room. The walls of the greenhouse were made of transparent glasses that did not obstruct sunlight. The length of daytime was 10-12 hrs per day during the plant growth. The light intensity measured at noon ranged from 8000 lumens on a cloudy day to 20,000 lumens on a sunny day. The temperature in the greenhouse was 22-30 °C during the day and 18-25 °C at night. Plants were watered every other day with 2 L of water to keep the soil moisture above 2 on a 0 to 10 scale, in which 0 meant completely dry soil and 10 meant soil saturated with water.

(a) First Greenhouse Set-up

(b) Second Greenhouse Set-up

Figure 6. Greenhouse for crop cultivation

3.2.2 Soil analysis

Soil samples were collected before planting and after harvesting from the second greenhouse experiment. Soil heavy metal contaminants including Al, Fe, Zn, Ni, Pb, As, Cd, Cr, Se, Co, Cu, and Hg were analyzed following EPA Method 3051A [68]. All soil samples were dried, ground and sieved to 177 µm (80 mesh). Then, 0.5 g of each of the soil samples was mixed with a digestive solution consisting of 9 mL 65% HNO3 and 3 mL 35% HCl, and was digested in a CEM Model 5 Microwave Digestion System at 800 W for 15 minutes at 170 °C. The sample extracts were subsequently passed through 450 nm mixed cellulose ester filters before being analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). Metal concentration in the extract solution was finally converted to soil metal concentration.

3.2.3 Plant analysis

Entire plants were collected at the end of the growth cycle of the second greenhouse experiment. The plants were washed and air-dried before they were separated into root, stem, leaf, and grain/seed head. Different parts of the plants were subsequently analyzed for their Al, Fe, Zn, Ni, Pb, As, Cd, Cr, Se, Co, Cu, and Hg concentrations using the same method as in the soil analysis.

3.2.4 Water analysis

Water analysis was done in the study. Sample collection was done in the second greenhouse experiment every one or two weeks as the plants grew. The samples were collected as soon as water leached out the pots after irrigation. ICP-OES was used to determine the Al, Fe, Zn, Ni, Pb, As, Cd, Cr, Se, Co, Cu, and Hg concentrations in the water samples.

3.3 Results and Discussion

3.3.1 Biomass production

No plant generated seeds in the first cultivation experiment due to the conditions in the greenhouse that limited plant growth. All plants except canola generated seeds at the end of the second cultivation experiment. Table 7 summarized the average dry mass of each part of an individual plant obtained from the control pots containing commercial topsoil and pots consisting of 90% w/w mine refuse and 10% w/w bauxite residues (MA). The data indicated that the dry mass of plants grown on MA could achieve no less than 60% of that on regular topsoil.

Table 7. Plant Dry Mass Obtained from the Greenhouse

Unit: g	Control				MA			
	Root	Stem	Leaf	Seed	Root	Stem	Leaf	Seed
Camelina	4.3	7.8*		5.8	3.1	6.8*		5.7
Canola	19.2	31.2	26.1	N.S.	18.9	17.7	24.2	N.S.
Sunflower	11.2	16.2	14.3	19.4	8.6	14.6	12.9	13.7
Sorghum	10.4	26.3	12.2	21.6	7.0	17.9	8.7	15.3

* Sum of the mass of stem and leaf
N.S. = no seed

3.3.2 Heavy metals in the soil

The data in Table 8 showed the heavy metal content in the soils used to grow biofuel crops in the greenhouse. Except for Hg, the heavy metal levels were quite consistent before and after plant growth with a difference no more than 35%.

Table 8。 Heavy Metal Content in Soil

	Unit: ppm		Al	Fe	Zn	Ni	Pb	As
Camalina	Soil	Before Planting	449726	929354	1179	363	326	<1
		After harvest	390383	760322	994	326	313	<1
	MA	Before Planting	231079	587410	423	219	420	<1
		After harvest	218179	640393	343	186	291	<1
Canola	Soil	Before Planting	449726	929354	1179	363	326	<1
		After harvest	465094	958491	1264	413	358	<1
	MA	Before Planting	197617	533943	361	187	349	<1
		After harvest	201822	474374	422	239	335	<1
Sunflower	Soil	Before Planting	449726	929354	1179	363	326	<1
		After harvest	439045	767322	973	315	277	<1
	MA	Before Planting	232763	966194	384	218	462	<1
		After harvest	213089	826114	357	204	356	<1
Sorghum	Soil	Before Planting	449726	929354	1179	363	326	<1
		After harvest	547685	981227	1300	420	361	<1
	MA	Before Planting	183443	686885	317	168	406	<1
		After harvest	246046	752103	377	211	333	<1
	Unit: ppm		Cd	Cr	Se	Co	Cu	Hg
Camalina	Soil	Before Planting	6.0	848	39	209	1154	31
		After harvest	5.0	724	13	187	741	4
	MA	Before Planting	10.1	625	61	118	431	36
		After harvest	5.3	535	43	98	372	7
Canola	Soil	Before Planting	6.0	848	39	209	1154	31

		After harvest	5.7	913	<0.01	245	794	13
	MA	Before Planting	5.5	569	33	96	343	23
		After harvest	6.0	568	52	118	378	10
Sunflower	Soil	Before Planting	6.0	848	39	209	1154	31
		After harvest	4.2	713	8	186	589	29
	MA	Before Planting	6.3	621	58	94	424	26
		After harvest	5.3	555	52	89	412	11
Sorghum	Soil	Before Planting	6.0	848	39	209	1154	31
		After harvest	5.6	939	8	245	790	13
	MA	Before Planting	6.6	589	71	81	320	37
		After harvest	5.6	547	40	101	489	6

3.3.3 Heavy metals in the plant

The results of plant analysis showed that crops grown on MA could take up 10-40% more heavy metals than those grown on regular soil and the metal concentration was 2-20 times higher in root, stem and leaf than in seed (Table 9a and b). The metal concentration in sorghum, which had the highest biomass yield among the four crops tested, showed a consistent decreasing trend from root to seed. The heavy metal in sorghum seeds from pots containing MA was low and similar to those grown on regular soil. This implied that sorghum grown on MA might be a suitable candidate for biofuel purposes.

Table 9a. Al, Fe, Zn, Ni, Pb and As Content in Plant

Unit: ppm			Al	Fe	Zn	Ni	Pb	As
Camelina	Soil	Root	5866	8.8	235	28	5.7	<1
		Stem & Leaf	566	5.9	75	25	4.7	<1
		Seed	112	0.4	17	11	1.1	<1
	MA	Root	8943	13.1	300	40	6.9	2.1
		Stem & Leaf	872	5.5	107	31	8.5	<1
		Seed	568	1.5	14	38	<1	0.6
Canola	Soil	Root	1076	1.2	73	8	2.5	3.2
		Stem	987	1.1	38	3	<1	2.5
		Leaf	8611	12.5	108	16	6.4	<1
	MA	Root	9457	14.1	120	37	11.0	<1
		Stem	1019	1.5	95	19	0.3	0.4
		Leaf	4936	7.5	132	36	2.0	3.1

Sunflower	Soil	Root	3084	35.7	129	25	14.9	<1
		Stem	182	0.2	34	1	<1	<1
		Leaf	460	0.5	117	2	<1	0.6
		Seed	162	0.2	109	4	<1	0.2
	MA	Root	3490	16.0	233	31	9.9	1.8
		Stem	790	0.4	105	22	0.7	0.4
		Leaf	2855	5.4	181	20	6.8	<1
		Seed	1812	2.5	214	64	1.1	<1
Sorghum	Soil	Root	8663	9.8	85	13	4.6	<1
		Stem	592	0.6	80	2	<1	<1
		Leaf	549	0.6	114	1	<1	1.0
		Seed	897	0.8	64	3	<1	<1
	MA	Root	2921	7.4	227	147	9.8	0.2
		Stem	225	0.4	290	152	0.1	1.4
		Leaf	658	1.2	142	132	<1	1.9
		Seed	107	2.5	83	10	1.1	<1

Table 9b. Cd, Cr, Se, Co, Cu, and Hg Content in Plant

Unit: ppm			Cd	Cr	Se	Co	Cu	Hg
Camelina	Soil	Root	2.2	13.2	17.8	8.9	<1	<1
		Stem & Leaf	1.2	8.7	4.8	4.7	<1	<1
		Seed	0.2	0.2	2.9	0.3	<1	<1
	MA	Root	3.3	19.0	31.1	10.8	<1	<1
		Stem & Leaf	2.5	10.5	8.1	8.8	<1	<1
		Seed	0.1	1.2	17.9	1.7	<1	<1
Canola	Soil	Root	0.4	6.3	5.3	0.7	55	1.4
		Stem	0.4	6.4	1.4	0.7	15	<1
		Leaf	0.9	39.5	<1	5.7	67	<1
	MA	Root	0.9	20.6	6.9	17.1	72	<1
		Stem	0.8	2.4	5.6	2.9	29	1.6
		Leaf	1.1	11.1	7.3	17.4	60	<1
Sunflower	Soil	Root	0.8	20.8	2.4	14.4	99	0.3
		Stem	0.2	1.6	<1	0.5	29	0.3
		Leaf	1.1	2.9	4.6	0.9	91	<1
		Seed	0.8	4.1	0.6	1.0	71	<1
	MA	Root	1.1	3.2	17.3	20.0	157	1.5
		Stem	1.2	0.8	8.1	14.8	39	2.1
		Leaf	2.5	3.9	10.1	14.3	111	<1
		Seed	1.8	2.4	10.7	23.1	76	<1
Sorghum	Soil	Root	1.5	21.5	6.1	10.8	71	0.8

		Stem	1.1	4.9	8.0	0.5	22	<1
		Leaf	1.0	3.9	<1	0.9	31	<1
		Seed	<1	3.7	2.9	0.1	29	<1
	MA	Root	4.2	6.5	8.8	7.5	62	1.8
		Stem	4.2	3.2	1.3	2.0	28	3.3
		Leaf	4.3	5.2	9.0	2.6	41	<1
		Seed	0.7	1.1	6.6	1.2	48	<1

3.3.4 Heavy metals in leachate

The heavy metal concentration in leachate collected 4 and 12 weeks after planting was summarized in Table 10. The heavy metal concentration in the leachate from the pots containing MA were only 1-30% of that of the leachate from pots filled with only mine refuse. In the meantime, the metal concentration in leachate from MA pots decreased faster than that from mine refuse pots. The lower and more quickly decreasing metal levels in leachate from MA pots could be attributed to the addition of 10%w/w bauxite residues which raised the soil pH from below 0 in pots containing only mine refuse to 5.1-7.1 in MA pots. The leachate analysis results demonstrated that bauxite residues were able to inhibit heavy metal contaminants in AML entering the environment with water flows.

Table 10. Heavy Metal Concentration in Leachate

Soil Type	**Plant**	**Week after planting**	**Heavy Metal Contaminant (ppm)**					
			Al	Fe	Zn	Ni	Pb	As
Mine refuse	No plant	4	2006	29.69	25.85	7.162	0.0142	<0.01
		12	1961	17.56	25.29	6.553	0.0107	<0.01
MA	Camelina	4	783.9	2.762	6.339	3.63	0.0403	<0.01
		12	394	1.04	2.65	5.442	0.0308	<0.01
MA	Canola	4	823	4.55	0.655	0.808	0.0354	<0.01
		12	290	2.97	0.758	0.324	0.0709	<0.01

MA	Sunflower	4	481	1.066	1.928	1.522	0.0452	<0.01
		12	238	0.4592	1.233	1.127	0.0439	<0.01
MA	Sorghum	4	572	2.0147	0.5346	0.49	0.0267	<0.01
		12	267	1.1011	0.7815	0.9913	0.0448	<0.01
Soil Type	**Plant**	**Week after planting**	**Heavy Metal Contaminant (ppm)**					
			Cd	Cr	Se	Co	Cu	Hg
Mine refuse		4	0.1215	0.3252	0.2085	2.872	9.552	<0.001
		12	0.1222	0.1492	0.219	2.782	7.739	<0.001
MA	Camelina	4	0.0674	0.0593	0.1312	1.481	3.394	<0.001
		12	0.0971	0.1428	0.154	2.314	8.048	<0.001
MA	Canola	4	0.0128	0.8	0.1298	0.2544	0.1226	0.002
		12	0.03	0.2676	0.0573	0.4177	0.7638	<0.001
MA	Sunflower	4	0.0264	0.0126	0.0641	0.5265	0.6707	<0.001
		12	0.0228	0.004	0.1019	0.355	0.2998	0.0016
MA	Sorghum	4	0.0061	0.0005	0.2415	0.1882	0.1515	0.0035
		12	0.0141	0.0002	0.3107	0.3141	0.1454	<0.001

3.4 Conclusions

Results from the greenhouse experiments showed that addition of bauxite residues that neutralized acidic mine refuse were a necessary step to enable plant growth. Plants grown on soil containing mine refuse had total metal concentrations 10-50% higher than those grown on commercial topsoil, but the metal levels in the seeds were less than 10% different between plants grown on soil and the mixture of mine refuse and bauxite residues. Bauxite residue addition and plant growth could effectively reduce the amount of contaminants that entered the environment with water flows. This research provided some evidences that growing biofuel crops could be a useful management for AMLs and an opportunity for valuable use of these degraded lands.

CHAPTER 4 – CONCLUSIONS AND FUTURE WORK

The management of urban marginal land and AML is a challenge that involves social, economic and environmental dimensions. The traditional methods for managing these marginal lands are either costly and have ranges of effectiveness. Biofuel feedstock production is proposed in this thesis to be an alternative to both enhance beneficial use of these lands and reduce the inputs to land management. The results from this study provided evidences on the viability of aligning biofuel production with land management. The urban marginal land biofuel system was conducted in collaboration with a non-profit organization, GTECH Strategies of Pittsburgh, PA, and involves extensive community participation. Since the urban marginal land biofuel system is built in collaboration with a non-profit organization and involves extensive community participation, this research presented an example of tying academia and the public towards an effort to solve an engineering challenge. The AML biofuel study investigates the beneficial use of wastes materials from the aluminum mining industry. The approach used in this investigation contributed intellectual merit to the broader understanding of the process of developing sustainable industrial systems.

While this study used experiments and life cycle methods to demonstrate the advantage of using marginal land for biofuels, the facts that the experiments were implemented under well-defined conditions and that the life cycle analysis only focused on energy analysis could be limitations for the results of this study to be applied to a broader range of scenarios. In the future, experiments at various locations and under different conditions, and life cycle assessments concerning more complete impact categories are needed to finish a comprehensive assessment of the sustainability of biofuel production on urban marginal land and AML.

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APPENDIX A

SOIL ANALYSIS RESULTS

Table A. Soil Analysis Results for the 0.8 ha-Brownfield

	Al					Fe				
Residential MSC (0-15 feet)	190000					66000				
Non-residential MSC (Surface Soil, 0-2 feet)	190000					190000				
	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011
Average (ppm)	65789	52182	60017	54040	56602	**171786**	**163144**	**131921**	**149479**	**187306**
Max. (ppm)	80597	71921	84700	79379	65797	**201241**	**226248**	**179903**	**218897**	**305451**
Min. (ppm)	50455	39323	40137	27435	47940	**139393**	**115896**	**66257**	**73380**	**123336**
Control (ppm)	64392	66786	62163	66643	69853	**140188**	**147890**	**146256**	**142580**	**140009**
	Zn					Ni				
Residential MSC (0-15 feet)	66000					4400				
Non-residential MSC (Surface Soil, 0-2 feet)	190000					56000				
	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011
Average (ppm)	633	794	642	763	922	209	174	134	117	221
Max. (ppm)	787	1116	1598	2258	2190	381	271	739	176	329
Min. (ppm)	363	522	258	25	546	151	127	17	77	128
Control (ppm)	588	621	635	609	601	145	159	161	149	159
	Pb					As				
Residential MSC (0-15 feet)	500					12				
Non-residential MSC (Surface Soil, 0-2 feet)	1000					53				
	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011
Average (ppm)	375	489	238	371	492	7.0	8.9	9.7	8.4	5.2
Max. (ppm)	**765**	**914**	266	460	**1151**	10.4	**16.6**	**13.4**	**13.4**	8.7
Min. (ppm)	170	220	209	250	215	4.4	4.9	5.2	4.5	1.4
Control (ppm)	432	413	409	427	414	9.0	9.3	9.5	9.1	9.8
	Cd					Cr				
Residential MSC (0-15 feet)	47					660				

Non-residential MSC (Surface Soil, 0-2 feet)	210					8400				
	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011
Average (ppm)	1.1	1.3	0.8	0.8	1.1	144	170	147	157	117
Max. (ppm)	3.6	5.4	1.4	1.5	2.3	280	293	387	209	173
Min. (ppm)	0.4	0.3	0.2	0.4	0.5	111	70	85	87	70
Control (ppm)	1.3	1.3	1.1	1.4	1.4	155	157	152	160	149

	Se				
Residential MSC (0-15 feet)	1100				
Non-residential MSC (Surface Soil, 0-2 feet)	14000				
	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011
Average (ppm)	4.9	3.1	3.0	3.6	5.9
Max. (ppm)	6.3	5.7	5.4	5.3	8.7
Min. (ppm)	3.5	1.7	1.6	1.9	2.8
Control (ppm)	5.1	5.5	4.9	5.4	5.6

Note: The concentrations that exceed the residential MSCs are highlighted in bold black; the concentrations that exceed the non-residential MSCs are highlighted in bold red.

Table B. Soil Analysis Results for the 0.12 ha-Greyfield

	Al					Fe				
Residential MSC (0-15 feet)	190000					66000				
Non-residential MSC (Surface Soil, 0-2 feet)	190000					190000				
	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011
Average (ppm)	65827	70149	63296	56455	66098	**144146**	**168891**	**139026**	**126248**	**162134**
Max. (ppm)	77775	77755	82218	58756	77259	**182256**	**334449**	**169444**	**155704**	**198114**
Min. (ppm)	51445	48050	36039	40473	47410	**114666**	**129202**	**87941**	**101786**	**114198**
Control (ppm)	54897	55786	54122	55987	54628	**133456**	**135773**	**139862**	**135673**	**131123**
	Zn					Ni				
Residential MSC (0-15 feet)	66000					4400				
Non-residential MSC (Surface Soil, 0-2 feet)	190000					56000				
	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011
Average (ppm)	591	825	772	711	660	142	169	115	95	165
Max. (ppm)	1126	2005	2845	2677	1557	182	387	175	150	250
Min. (ppm)	418	404	257	91	427	105	124	52	63	102
Control (ppm)	528	564	587	534	555	156	141	155	152	147
	Pb					As				
Residential MSC (0-15 feet)	500					12				
Non-residential MSC (Surface Soil, 0-2 feet)	1000					53				
	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011
Average (ppm)	**510**	**685**	**522**	340	**536**	5.5	9.4	8.0	6.7	5.2
Max. (ppm)	**1194**	**1719**	**1457**	**1140**	**1259**	7.2	**13.9**	**16.1**	9.4	7.0
Min. (ppm)	214	248	160	91	183	4.5	3.3	2.8	4.4	2.9
Control (ppm)	399	410	411	401	418	7.7	7.1	7.9	7.7	7.1
	Cd					Cr				
Residential MSC (0-15 feet)	47					660				

Non-residential MSC (Surface Soil, 0-2 feet)	210					8400				
	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011
Average (ppm)	0.6	0.9	0.7	0.8	0.7	111	164	127	126	125
Max. (ppm)	1.4	2.3	1.4	2.0	1.2	154	258	179	202	294
Min. (ppm)	0.3	0.3	0.3	0.4	0.4	76	57	83	99	82
Control (ppm)	0.5	0.5	0.6	0.6	0.6	121	113	115	120	119
	Se					Note: The concentrations that exceed the residential MSCs are highlighted in bold black; the concentrations that exceed the non-residential MSCs are highlighted in bold red.				
Residential MSC (0-15 feet)	1100									
Non-residential MSC (Surface Soil, 0-2 feet)	14000									
	Jun. 10, 2008	Oct. 7, 2009	May 24, 2010	Sep. 13, 2010	Jul. 19, 2011					
Average (ppm)	4.2	3.4	2.8	3.9	3.9					
Max. (ppm)	6.9	6.9	4.1	13.1	4.6					
Min. (ppm)	2.9	0.6	1.1	2.0	2.9					
Control (ppm)	4.3	4.5	4.7	4.4	4.1					

APPENDIX B

ENERGY CALCULATIONS FOR THE URBAN MARGINAL LAND BIOFUEL SYSTEM

Energy Balance Calculation (Unallocated)

<u>0.8 ha-Brownfield:</u>

Field Preparation:

Table 2, Equation 2: Mowing and tilling = 7.6 L gasoline[a] × 32.3 MJ/L[b] ÷ 90.6%[c] = 270.9 MJ

Table 2, Equation 3: Transport[d] = 12 km[e] ÷ (7.6 km/L)[f] × 32.3 MJ/L[b] ÷ 90.6%[c] = 56.3 MJ

Transport[d]:

Table 2, Equation 4: Transport within Pittsburgh = 12 km[e] ÷ (7.6 km/L)[f] × 32.3 MJ/L[b] ÷ 90.6%[c] = 56.3 MJ

Table 2, Equation 5: Transport to and from University Park = [(217.6 km[g] × 2) ÷ (10.1 km/L)[h]] × [(0.3024 m^3)[i] × (735 kg/m^3)[j] ÷ 1000 kg[k]] × 32.3 MJ/L[b] ÷ 90.6%[c] = 341.4 MJ

Biofuel Processing:

Table 2, Equation 6: Sunflower oil extraction = (0.3024 m^3)[i] × (735 kg/m^3)[j] ÷ 50 kg/hr[l] × (2.2 kW[m] × 3.6 MJ/kWh) ÷ 46.0%[n] = 76.5 MJ

Table 2, Equation 7: Sunflower oil to biodiesel = (23.8 L/ha[o] × 0.8 ha[p] × 0.919 kg/L[q] ÷ 1.04[r]) × 5.8 MJ/kg of biodiesel[s] = 97.6 MJ

Biofuel Distribution:

Table 2, Equation 8: Transportation and distribution of biodiesel = (23.8 L/ha[o] × 0.8 ha[p] × 0.919 kg/L[q] ÷ 1.04[r]) × (38.4 MJ/kg[t] × 8982 J/MJ[u] ÷ 1000000J/MJ) = 5.8 MJ

Energy Output:

Table 2, Equation 9: Biodiesel = (23.8 L/ha[o] × 0.8 ha[p] × 0.919 kg/L[q] ÷ 1.04[r]) × 38.4 MJ/kg[t] = 646.1 MJ

Table 2, Equation 10: Sunflower meal = (23.8 L/ha[o] × 0.8 ha[p] × 0.919 kg/L[q]) × (660/340)[v] × 9.5 MJ/kg[w] =322.7 MJ

Table 2, Equation 11: Glycerin = (23.8 L/ha[o] × 0.8 ha[p] × 0.919 kg/L[q] ÷ 1.04[r] × 0.214[x]) × 18.6 MJ/kg[y] = 67.0 MJ

[a] Fuel consumption value from GTECH Strategies;
[b] Low heating value of conventional gasoline reported by GREET1_2011;
[c] Refining efficiency for conventional gasoline reported by GREET1_2011;
[d] Calculation based on GMC Canyon 1-ton pickup;
[e] Average distance travelled by GTECH to and from its plots;
[f] Fuel efficiency of GMC Canyon 1-ton pickup in city driving;
[g] Distance between Pittsburgh and University Park, PA;
[h] Fuel efficiency of GMC Canyon 1-ton pickup on the highway;
[i] Seeds output from the 0.8 ha-Brownfield;
[j] Density of sunflower seeds [72];
[k] Load capacity of GMC Canyon 1-ton pickup;
[l] Processing capability of a typical oilseed crusher for sunflower seeds [73];

[m] Power of the oilseed crusher [73];
[n] Power plant energy conversion efficiency based on GREET1_2011 and fuel mix to generate electricity in the western Pennsylvania;
[o] Sunflower oil yield reported by GTECH Strategies;
[p] Area of the 0.8 ha-Brownfield;
[q] Density of sunflower oil [82];
[r] Conversion ratio from bio-oil to biodiesel reported by GREET1_2011;
[s] Energy consumption in the transesterification process reported by GREET1_2011;
[t] Lower heating value of sunflower biodiesel [74];
[u] Energy consumption for biodiesel transportation and distribution reported by GREET1_2011.
[v] Mass-based ratio of sunflower meal and sunflower oil from sunflower seeds [75];
[w] Metabolizable energy content in sunflower meal [75, 76];
[x] Mass-based ratio of glycerin and biodiesel from biodiesel production process given by GREET1_2011;
[y] Energy content of glycerin reported by GREET1_2011.

0.12 ha-Greyfield:
Field Preparation:
Table 2, Equation 2: Mowing and tilling = 1.1 L gasoline[a] × 32.3 MJ/L[b] ÷ 90.6%[c] = 39.2 MJ
Table 2, Equation 3: Transport[d] = 12 km[e] ÷ (7.6 km/L)[f] × 32.3 MJ/L[b] ÷ 90.6%[c] = 56.3 MJ

Transport[d]:
Table 2, Equation 4: Transport within Pittsburgh = 12 km[e] ÷ (7.6 km/L)[f] × 32.3 MJ/L[b] ÷ 90.6%[c] = 56.3 MJ
Table 2, Equation 5: Transport to and from University Park = [(217.6 km[g] × 2) ÷ (10.1 km/L)[h]] × [(0.04536 m^3)[i] × (735 kg/m^3)[j] ÷ 1000 kg[k]] × 32.3 MJ/L[b] ÷ 90.6%[c] = 51.2 MJ

Biofuel Processing:
Table 2, Equation 6: Sunflower oil extraction = (0.04536 m^3)[i] × (735 kg/m^3)[j] ÷ 50 kg/hr[l] × (2.2 kW[m] × 3.6 MJ/kWh) ÷ 46.0%[n] = 11.5 MJ
Table 2, Equation 7: Sunflower oil to biodiesel = (23.8 L/ha[o] × 0.12 ha[p] × 0.919 kg/L[q] ÷ 1.04[r]) × 5.8 MJ/kg of biodiesel[s] = 14.6 MJ

Biofuel Distribution:
Table 2, Equation 8: Transportation and distribution of biodiesel = (23.8 L/ha[o] × 0.12 ha[p] × 0.919 kg/L[q] ÷ 1.04[r]) × (38.4 MJ/kg[t] × 8982 J/MJ[u] ÷ 1000000J/MJ) = 0.9 MJ

Energy Output:
Table 2, Equation 9: Biodiesel = (23.8 L/ha[o] × 0.12 ha[p] × 0.919 kg/L[q] ÷ 1.04[r]) × 38.4 MJ/kg[t] = 96.9 MJ
Table 2, Equation 10: Sunflower meal = (23.8 L/ha[o] × 0.12 ha[p] × 0.919 kg/L[q]) ×

(660/340)[v] × 9.5 MJ/kg[w] = 48.4 MJ
Table 2, Equation 11: Glycerin = (23.8 L/ha[o] × 0.12 ha[p] × 0.919 kg/L[q] ÷ 1.04[r] × 0.214[x]) × 18.6 MJ/kg[y] = 10.0 MJ

[a] Fuel consumption value from GTECH Strategies;
[b] Low heating value of conventional gasoline reported by GREET1_2011;
[c] Refining efficiency for conventional gasoline reported by GREET1_2011;
[d] Calculation based on GMC Canyon 1-ton pickup;
[e] Average distance travelled by GTECH to and from its plots;
[f] Fuel efficiency of GMC Canyon 1-ton pickup in city driving;
[g] Distance between Pittsburgh and University Park, PA;
[h] Fuel efficiency of GMC Canyon 1-ton pickup on the highway;
[i] Seeds output from the 0.12 ha-Greyfield;
[j] Density of sunflower seeds [72];
[k] Load capacity of GMC Canyon 1-ton pickup;
[l] Processing capability of a typical oilseed crusher for sunflower seeds [73];
[m] Power of the oilseed crusher [73];
[n] Power plant energy conversion efficiency based on GREET1_2011 and fuel mix to generate electricity in the western Pennsylvania;
[o] Sunflower oil yield reported by GTECH Strategies;
[p] Area of the 0.12 ha-Greyfield;
[q] Density of sunflower oil [82];
[r] Conversion ratio from bio-oil to biodiesel reported by GREET1_2011;
[s] Energy consumption in the transesterification process reported by GREET1_2011;
[t] Energy value of the sunflower biodiesel [74];
[u] Energy consumption for biodiesel transportation and distribution reported by GREET1_2011;
[v] Mass-based ratio of sunflower meal and sunflower oil from sunflower seeds [75];
[w] Metabolizable energy content in sunflower meal [75, 76];
[x] Mass-based ratio of glycerin and biodiesel from biodiesel production process given by GREET1_2011;
[y] Energy content of glycerin reported by GREET1_2011.

Energy Credits Calculation for Co-products
Market Value-based Allocation:
0.8 ha-Brownfield:
Market value of biodiesel = (23.8 L/ha[a] × 0.8 ha[b] × 0.919 kg/L[c] ÷ 1.04[d]) × \$1.03/kg[e] = \$17.3
Market value of sunflower meal = (23.8 L/ha[a] × 0.8 ha[b] × 0.919 kg/L[c]) × (660 kg meal / 340 kg sunflower oil)[f] × \$0.17/kg[g] = \$5.8
Market value of glycerin = (23.8 L/ha[a] × 0.8 ha[b] × 0.919 kg/L[c] ÷ 1.04[d] × 0.214[h]) × \$0.33/kg[i] = \$1.2

0.12 ha-Greyfield:

Market value of biodiesel = (23.8 L/ha[a] × 0.12 ha[j] × 0.919 kg/L[c] ÷ 1.04[d]) × \$1.03/kg[e] = \$2.6
Market value of sunflower meal = (23.8 L/ha[a] × 0.12 ha[j] × 0.919 kg/L[c]) × (660 kg meal / 340 kg sunflower oil)[f] × \$0.17/kg[g] = \$0.9
Market value of glycerin = (23.8 L/ha[a] × 0.12 ha[j] × 0.919 kg/L[c] ÷ 1.04[d] × 0.214[h]) × \$0.33/kg[i] = \$0.2

a. Sunflower oil yield reported by GTECH Strategies;
b. Area of the 0.8 ha-Brownfield;
c. Density of sunflower oil [82];
d. Conversion ratio from bio-oil to biodiesel reported by GREET1_2011;
e. Price of biodiesel given by GREET1_2011;
f. Mass-based ratio of sunflower meal and sunflower oil from sunflower seeds [75];
g. Average sunflower meal price between 2009 and 2010 [83];
h. Mass-based ratio of glycerin and biodiesel from biodiesel production process given by GREET1_2011;
i. Price of glycerin reported by GREET1_2011;
j. Area of the 0.12 ha-Greyfield.

Energy-based Allocation:
0.8 ha-Brownfield:
Energy content of biodiesel = (23.8 L/ha[a] × 0.8 ha[b] × 0.919 kg/L[c] ÷ 1.04[d]) × 38.4 MJ/kg[e] = 646.1 MJ
Energy content of sunflower meal = (23.8 L/ha[a] × 0.8 ha[b] × 0.919 kg/L[c]) × (660/340)[f] × 9.5 MJ/kg[g] = 322.7 MJ
Energy content of glycerin = (23.8 L/ha[a] × 0.8 ha[b] × 0.919 kg/L[c] ÷ 1.04[d] × 0.214[h]) × 18.6 MJ/kg[i] = 67.0 MJ

0.12 ha-Greyfield:
Energy content of biodiesel = (23.8 L/ha[a] × 0.12 ha[j] × 0.919 kg/L[c] ÷ 1.04[d]) × 38.4 MJ/kg[e] = 96.9 MJ
Energy content of sunflower meal = (23.8 L/ha[a] × 0.12 ha[j] × 0.919 kg/L[c]) × (660/340)[f] × 9.5 MJ/kg[g] = 48.4 MJ
Energy content of glycerin = (23.8 L/ha[a] × 0.12 ha[j] × 0.919 kg/L[c] ÷ 1.04[d] × 0.214[h]) × 18.6 MJ/kg[i] = 10.0 MJ

a. Sunflower oil yield reported by GTECH Strategies;
b. Area of 0.8 ha-Brownfield;
c. Density of sunflower oil [82];
d. Conversion ratio from bio-oil to biodiesel reported by GREET1_2011;
e. Lower heating value of sunflower biodiesel [74];
f. Mass-based ratio of sunflower meal and sunflower oil from sunflower seeds [75];
g. Metabolizable energy content in sunflower meal [75, 76];
h. Mass-based ratio of glycerin and biodiesel from biodiesel production process

given by GREET1_2011;
i. Energy content of glycerin reported by GREET1_2011;
j. Area of 0.12 ha-Greyfield.

Mass-based Allocation:

0.8 ha-Brownfield:

Mass of Biodiesel = 23.8 L/ha[a] × 0.8 ha[b] × 0.919 kg/L[c] ÷ 1.04[d] = 16.8 kg

Mass of sunflower meal = (23.8 L/ha[a] × 0.8 ha[b] × 0.919 kg/L[c]) × (660/340)[e] = 34.0 kg

Mass of glycerin = 23.8 L/ha[a] × 0.8 ha[b] × 0.919 kg/L[c] ÷ 1.04[d] × 0.214[f] = 3.6 kg

0.12 ha-Greyfield:

Mass of Biodiesel = 23.8 L/ha[a] × 0.12 ha[g] × 0.919 kg/L[c] ÷ 1.04[d] = 2.5 kg

Mass of sunflower meal = (23.8 L/ha[a] × 0.12 ha[g] × 0.919 kg/L[c]) × (660/340)[e] = 5.1 kg

Mass of glycerin = 23.8 L/ha[a] × 0.12 ha[g] × 0.919 kg/L[c] ÷ 1.04[d] × 0.214[f] = 0.5 kg

a. Sunflower oil yield reported by GTECH Strategies;
b. Area of 0.8 ha-Brownfield;
c. Density of sunflower oil [82];
d. Conversion ratio from bio-oil to biodiesel reported by GREET1_2011;
e. Mass-based ratio of sunflower meal and sunflower oil from sunflower seeds [75];
f. Mass-based ratio of glycerin and biodiesel from biodiesel production process given by GREET1_2011;
g. Area of 0.12 ha-Greyfield.

Displacement Method:

Energy credit for sunflower meal = (660 kg meal / 340 kg sunflower oil)[a] × (9.5 / 12.3)[b] × 1.9 MJ/kg[c] = 2.8 MJ/kg sunflower oil

Energy credit for glycerin = 19.6 MJ/kg biodiesel[d]

0.8 ha-Brownfield:

Energy credit for sunflower meal = (23.8 L/ha[e] × 0.8 ha[f] × 0.919 kg/L[g]) × 2.8 MJ/kg sunflower oil = 49.0 MJ

Energy credit for glycerin = (23.8 L/ha[e] × 0.8 ha[f] × 0.919 kg/L[g] ÷ 1.04[h]) × 19.6 MJ/kg biodiesel[d] = 329.8 MJ

0.12 ha-Greyfield:

Energy credit for sunflower meal = (23.8 L/ha[e] × 0.12 ha[i] × 0.919 kg/L[g]) × 2.8 MJ/kg sunflower oil = 7.3 MJ

Energy credit for glycerin = (23.8 L/ha[e] × 0.12 ha[i] × 0.919 kg/L[g] ÷ 1.04[h]) × 19.6 MJ/kg biodiesel[d] = 49.5 MJ

a. Mass-based ratio of sunflower meal and sunflower oil from sunflower seeds [75];
b. Ratio of metabolizable energy of sunflower meal and soy meal [75];
c. Energy displaced by soy meal given by GREET1_2011;

[d] Energy credit for glycerin production given by GREET1_2011;
[e] Sunflower oil yield reported by GTECH Strategies;
[f] Area of the 0.8 ha-Brownfield;
[g] Density of sunflower oil [82];
[h] Conversion ratio from bio-oil to biodiesel reported by GREET1_2011;
[i] Area of 0.12 ha-Greyfield.

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