"Only after the last tree has been cut down,
after the last river has been poisoned,
after the last fish has been caught,
only then will you realize that money cannot be eaten"

- Chief Seattle (1851)

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Environmental sustainability of biobased products: new assessment methods and case studies

Thesis submitted in fulfillment of the requirements for the degree of Doctor (PhD) in Applied Biological Sciences: Environmental Technology

Title in Dutch:

Milieuduurzaamheid van biogebaseerde producten: nieuwe evaluatiemethoden en casestudies

Alvarenga, R.A.F. (2013). Environmental sustainability of biobased products: new assessment methods and case studies. PhD thesis. Faculty of Bioscience Engineering, Ghent University, Belgium.

ISBN 978-90-5989-622-2

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ABBREVIATION INDEX

AoP	Area of protection
As	Arsenic
ASCII	American Standard Code for Information Interchange
BDP	Biodiversity damage potential
BLUM	Brazilian land use model
BOD5	Biochemical oxygen demand (5 days)
CaO	Calcium oxide
Cd	Cadmium
CED	Cumulative energy demand
CEENE	Cumulative exergy extraction from the natural environment
CEV	Chemical exergy value
CExC	Cumulative exergy consumption
CExD	Cumulative exergy demand
CF	Characterization factor
CFC-11 eq	Equivalents of trichlorofluoromethane
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
CO_2eq	Equivalents of carbon dioxide
Cr	Chromium
CTBE	Brazilian bioethanol science and technology laboratory
CTUe	Comparative toxic unit - ecotoxicity
CTUh	Comparative toxic unit - human toxicity
Cu	Copper
CV	Coefficient of variation

DALY	Disability-adjusted life year
dLUC	Direct land use change
DM	Dry matter
E100	Fuel with 100% of its volume of hydrous ethanol
E20	Fuel with 20% of its volume of anhydrous ethanol
E22	Fuel with 22% of its volume of anhydrous ethanol
E25	Fuel with 25% of its volume of anhydrous ethanol
ECEC	Ecological cumulative exergy consumption
EEA	European Environment Agency
ELCD	European Reference Life Cycle Database
gC	Grams of carbon
GHG	Greenhouse gases
GIS	Geographic information systems
GJ	Gigajoule (of energy)
GJ_{ex}	Gigajoule of exergy
H/A	Hierarchist version with average weighting set (of Recipe method)
H_2SO_4	Sulfuric acid
ha	Hectares
ha.yr	Hectares.years
HANPP	Human appropriation of net primary production
Hg	Mercury
HHV	High heating value
ICEC	Industrial cumulative exergy consumption
ILCD	International Reference Life Cycle Data System
iLUC	Indirect land use change
IPCC	Intergovernamental panel of climate change

ISO	International Organization for Standardization
K_2O	Potassium oxide
kg	Kilogram
kgC	Kilograms of carbon
kgDM	Kilograms of dry matter
kgNeq	Kilograms of nitrogen equivalent
kgPeq	Kilograms of phosphorous equivalent
kJ	Kilojoule (of energy)
kJ_{ex}	Kilojoule of exergy
km	Kilometers
L	Liters
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LHV	Low heating value
LUC	Land use change
m^2a	Squared meters.annum
m^3	Cubic meters
MJ	Megajoule (of energy)
MJ_{ex}	Megajoule of exergy
MW	Megawatt
N	Nitrogen
N_2O	Dinitrogen monoxide
NaOH	Sodium hydroxide
NEV	Net energy value
NH_3	Ammonia

Ni	Nickel
NMVOC	Non-methane volatile organic compounds
NO	Nitric oxide
NO_3	Nitrate
NO_X	Nitrogen oxides
NPP	Net primary production
NPP_{act}	Actual net primary production
NPP_{pot}	Potential (natural) net primary production
NPP_h	Harvested fraction of the net primary production
NPP_t	Remaining NPP (NPP - NPP_h)
P_2O_5	Phosphorus pentoxide
PAH	Polycyclic aromatic hydrocarbon
Pb	Lead
PED	Primary energy demand
PM_{10}	Particulate matter (< 10 micrometers)
PM_{10} eq	Equivalents of particulate matter (<10 micrometers)
$PM_{2,5}$	Particulate matter (< 2.5 micrometers)
Pt	Ecopoints
PVC	Polyvynil chloride
RAM	Resource accounting methodologies
Se	Selenium
SED	Solar energy demand
SF_6	Sulfur hexafluoride
SO_2	Sulfur dioxide
SOC	Soil organic carbon
SO_X	Sulfur oxides

ton	Metric ton
TSP	Total suspendended particules
U235eq	Equivalents of uranium-235
UNICA	Brazilian union of sugarcane industry
USLCI	United States Life Cycle Inventory database
VCM	Vynil chloride monomer
Zn	Zinc
ΔEP	Overall net annual exergy production
ΔNPP_{LC}	Effect of land use induced change in NPP

CHAPTER 1: Introduction

1.1 BIOBASED PRODUCTS

Biobased products are products that have their main feedstock coming completely (or partially) from biological origin, for instance agricultural crops and wood. They can be summarized in three levels of products: food & feed, biobased materials, and bioenergy (De Meester, 2013). It is important to state that biodegradable products and/or industrial products produced through biological processes may also be named as biobased products (or simply bio-products), but hereafter in this PhD Dissertation the terminology 'biobased products' shall refer to the former definition, which can be visualized in Figure 1.1.

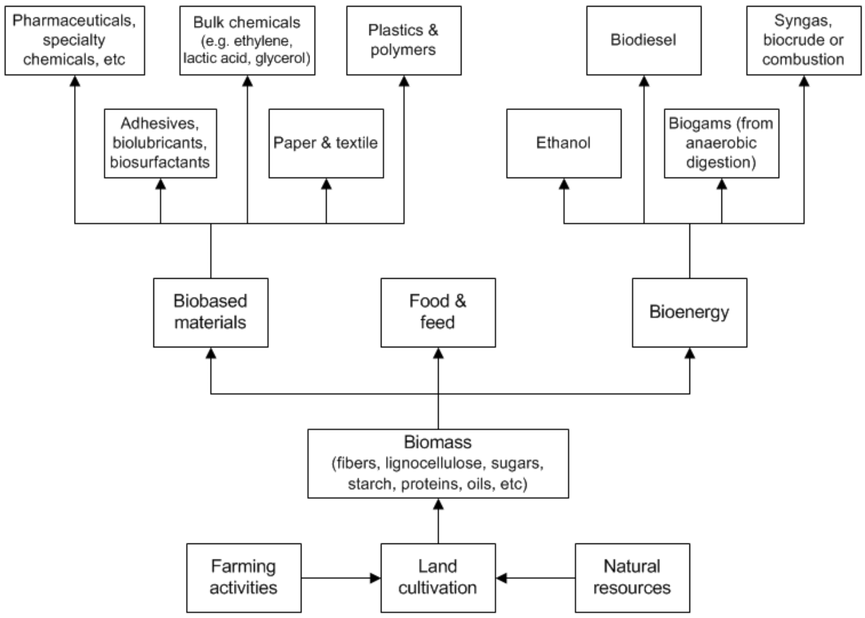

Figure 1.1: Visualization of three levels of biobased products (biobased materials, food & feed, and bioenergy), coming from biomass produced on a certain land (extracted from De Meester (2013))

Before the industrial revolution (until early 19th century) the World society was highly dependent on biobased products. For instance, natural fibers (e.g. cotton, wool, and silk) were used in textile materials for thousands of years and cow horn and ivory were used for more durable applications (e.g. musical instruments) (Shen, 2011). Biofuels were the main feedstock used for energy worldwide (e.g. wood and vegetable oils), as it can be seen in Figure 1.2. The growth in the consumption of fossil fuels began only in the second half of 19th century, starting with coal. During the 20th century, with the increase of large-scale oil extraction, the worldwide consumption of fossil fuels grew exponentially, while the growth of biofuels consumption was virtually stagnant (Figure 1.2). Following the same trend, materials started to be produced from fossil-based feedstocks (e.g., fossil-based plastics), while biobased materials were mainly used just as alternative for their respective fossil-based product, usually motivated by economic reasons, e.g. the subsidized production of biobased polyethylene in Brazil in the decade of 1980, after the oil crisis of 1970s (Shen, 2011). It is interesting to note that the curve of global energy consumption (Figure 1.2) follows the same trend of the curves of worldwide population growth, gross domestic product (GDP) growth, and GDP per capita growth (Figure 1.3), corroborating their interconnection.

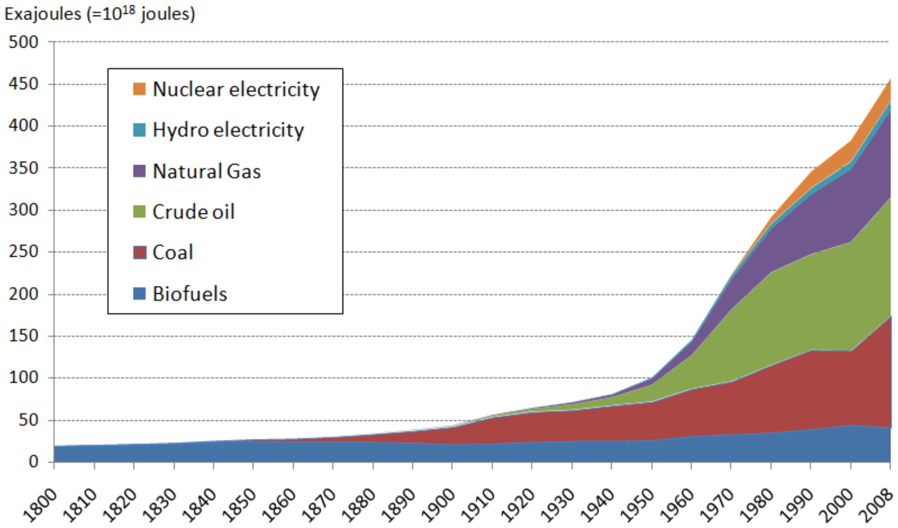

Figure 1.2: Global energy consumption between 1800 and 2008 (extracted from Smil (2010))

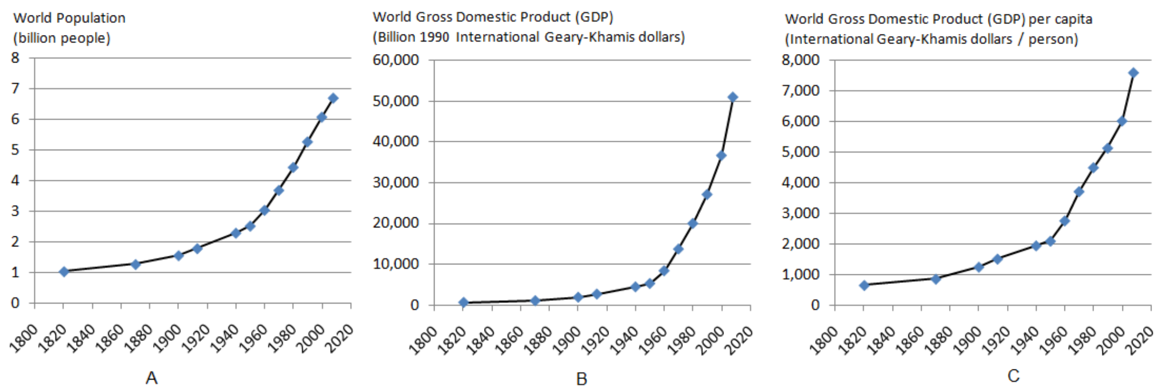

Figure 1.3: Population growth (A), Gross domestic product (GDP) growth (B) and GDP per capita growth between 1820 and 2008 (extracted from Maddison (2010))

Warr et al. (2010) studied the evolution on consumption of energy and materials (in exergy terms) between 1900 and 2000 for four particular countries: United States of America (USA), Japan, Austria, and United Kingdom. As we can see in Figure 1.4, the values differ among the countries, but the trend is similar, i.e., growth in the consumption of fossil-based products with time and a virtual stagnant consumption of biobased products.

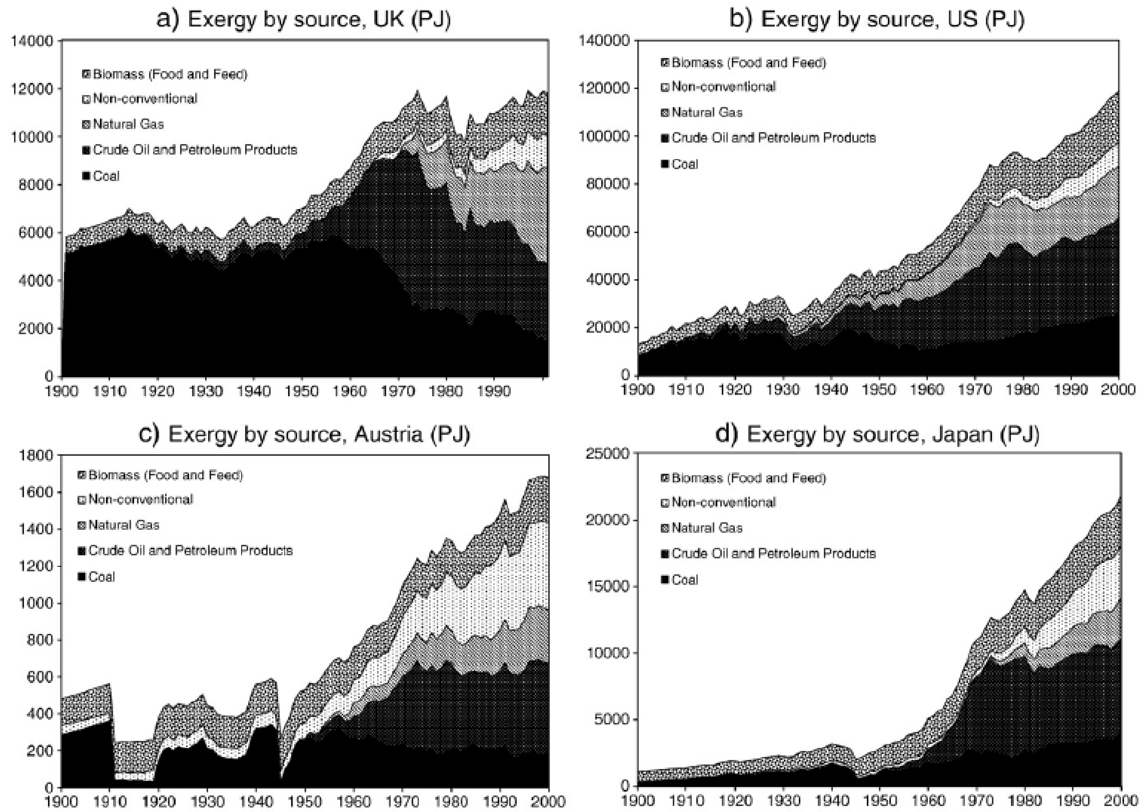

Figure 1.4: Exergy inputs by source between 1900 and 2000, for United Kingdom (a), United States of America (b), Austria (c), and Japan (d). Note that wood (as fuel) is included in biomass grouping (extracted from Warr et al. (2010))

This increased consumption in fossil-based feedstock (for fuel and materials) led to several environmental problems, including climate change impacts, the depletion of fossil natural resources, inappropriate waste management, among others. Concerned with these environmental issues, governments took action into promoting the use of biobased products, for instance the Renewable Energy Directive from European Union (European commission, 2009). These actions allowed the renaissance of a more biobased economy (Langeveld et al., 2010; Mülhaupt, 2012; Shen et al., 2010), where energy and materials are mainly produced from biomass (Vandermeulen et al., 2011; Vandermeulen et al., 2012).

Even though this living shift from fossil-based to biobased economy is still in its infancy (Jenkins, 2008; Kircher, 2012; Vandermeulen et al., 2012), several products from different economic sectors can already be found in the current market. For instance, the production of bioethanol as biofuel, which has been produced from sugarcane for decades in Brazil, and in the USA the production (mainly from corn) increased from approximately 6 million cubic meters in 2000 to more than 50 million cubic meters in 2010 (RFA, 2012). Another example are biobased chemicals (e.g. polylactic acid), which global annual production is expected to raise from currently 2 to 15 million metric tons by 2020 (Reisch, 2012), and to reach between 17 and 38% of all organic chemical production by 2050 (IEA Bioenergy, 2012).

Some biobased products have been produced for a long time through traditional technologies, for instance paper and board and first generation bioethanol from sugarcane. On the other hand, the renaissance of the biobased economy gives support to products based on new technologies, which can be either applied to the agricultural stage (so-called green biotechnology) or to the industrial stage (so-called white biotechnology) (Hermann and Patel, 2007). Nevertheless, despite the level of technology of the biobased products (traditional, green biotechnology, or white technology), the availability of terrestrial biomass, and as a consequence the availability of land, is vital. In this sense, due to their vast and fertile land area, certain countries will play an important role in a biobased economy, for instance China, USA, Australia, and Brazil, countries with the largest agricultural areas in the World (FAO, 2012).

1.2 THE INTERFERENCE OF BIOBASED PRODUCTS WITH ECOSYSTEMS AND LAND

The importance of land availability in a biobased economy is clear, especially when considering that the share of biobased products in the market is expected to rise in the future (as previously mentioned). If, on top of that, we correlate this information with projections of the World's population to grow to more than 9 billion in 2050 (United Nations, 2009) and a growth rate of 5% of the Human Development Index from 1980 to 2010 (United Nations, 2010), we can conclude that an increased pressure on land is likely. For illustration, regarding solely production of biofuels, global land availability would have to increase from currently 30 Mha to approximately 100 Mha in 2050, in order to meet the biofuel targets for that year (IEA, 2011). This increased pressure on land comes along with several social, economical, and environmental issues (the three pillars of sustainability). An example of an economic issue is the expected increase in food prices due to land competition with biofuels (Rathmann et al., 2010), while one example of a social issue is the expropriation of land areas from indigenous populations (Assies, 2008; Socpa, 2010). However, in this PhD dissertation we focus on the environmental issues related to the biobased products, i.e., their impacts on ecosystems, land, and the environment as a whole.

1.2.1 Ecosystem services

Our current society lives under a complex economic system, in which different commodities are exchanged among different countries, through a globalized World. This system allows countries with low natural resources to provide certain products (e.g. feed for livestock) to their population by importing goods. In these cases, even though these natural resources are not produced in the country where they are consumed, they are somehow still extracted from the ecosphere and brought to the technosphere/anthroposphere. Therefore, it is straightforward to conclude that humans highly depend on the services provided by ecosystems.

Ecosystem services have been studied for decades, but only in 2005 it has been standardized by the United Nations in a report named Millennium Ecosystem Assessment (MEA, 2005). This report categorizes the ecosystem services in four classes:

- Provisioning services, such as food, wood and fiber, fuel, and freshwater;
- Regulating services, such as flood control, climate regulation, and water purification;
- Supporting services, such as nutrient cycling, soil formation, and primary production;
- Cultural services, such as spiritual, aesthetic, recreational, and educational benefits.

Even though this report has the perception of ecosystem services from the humankind point of view (since it was written by humans), it is an important guidance to reach environmental sustainability. On top of that, it allowed a popularization of the term ‘ecosystem services’, making the link with other environmental sciences easier. For instance, prior to that report the terminologies used in life cycle assessment (LCA) for the land use impacts, other than biodiversity loss, were diverse (e.g. *life support functions*) (Lindeijer, 2000a, b); while nowadays the terminology ecosystem services is rather agreed upon (Koellner and Geyer, 2013; Saad et al., 2013).

1.2.2 Land use and land use impacts

As previously mentioned, the raise of a biobased economy is expected to come along with an increased pressure on land, regardless its potential benefits to climate change, causing several environmental impacts (so-called land use impacts). Therefore, it is important to clarify certain terminologies regarding land use and land use impacts:

- *Land use* (or land occupation), defined as "*the arrangements, activities and inputs people undertake in a certain land cover type to produce, change or maintain it*" (FAO, 1997), refers to the human use of a certain area, for a certain purpose and a certain time, and it is commonly represented through units of area and time (e.g. ha.yr).
- Another common terminology is *land use change* (LUC), or land transformation, which refers to the change (by humans) of the characteristics of a certain land (e.g. flora, fauna, soil, soil surface), from its original state to an altered state (Weidema and Lindeijer, 2001). These changes can be substantial, for instance the deforestation of a natural tropical rainforest for agricultural purposes, or more subtle, for instance the change from intensive to extensive agriculture production. When studying the LUC caused by a product (during agricultural or forestry practices), the direct LUC (dLUC) can be easily observed, as it is the change that occurred at the site where it is produced. However, a product might be inducing a LUC that can be happening outside of its local boundaries, and in this case they are commonly named as indirect LUC (iLUC) (Gnansounou et al., 2008). For illustration, let's consider that potatoes used to be produced at a certain land area 'X', but due to a high market demand of biofuels this area switches from potatoes to maize production. In this simple case, there is a dLUC from potato to maize production. However, the demand for potato (for food purposes) would still exist, and it could start to be supplied by imported potatoes, which (in our simple example) can be considered to be produced in an area 'Y' that used to be natural grasslands. Then, if this cause-and-effect chain is verified, we can say that apart from the dLUC abovementioned, the maize produced in that certain area 'X' is also causing an iLUC from natural grasslands to potato production (at the area 'Y'). Nevertheless, the evaluation of iLUC from a specific product is not so straightforward in reality (Adami et al., 2012; Eurpean Commission, 2010).
- Moreover, land use and LUC (dLUC or iLUC) may cause impacts to the environment, which are commonly called as *land use impacts*. Numerous land use impacts can exist

depending on the product analyzed and its location, for instance the loss of biodiversity due to dLUC of a tropical rainforest to soybean cultivation. Other types of impacts are those affecting the ecosystem services (MEA, 2005), for instance the loss of natural water purification services (one type of regulating services) supplied by ecosystems, due to land use activities causing soil compaction, which can decrease the groundwater recharge (Saad et al., 2011).

Land plays an important role for the evaluation of environmental impacts of biobased products. Furthermore, the shift from traditional fossil-based to biobased products may raise also environmental impacts other than land use impacts, e.g. higher ecotoxicity from the emission of pesticides into groundwater. Therefore, in order to provide valuable information, it can be brought to light that the environmental impacts (and benefits) of biobased products should be analyzed through holistic environmental assessment methodologies, based on a life cycle perspective.

1.3 ENVIRONMENTAL SUSTAINABILITY ASSESSMENT METHODOLOGIES FOR (BIOBASED) PRODUCTS

In order to assess the environmental sustainability of a certain product (biobased or not), it is essential to use environmental sustainability assessment methodologies, and the most predominant is LCA (Dewulf and Van Langenhove, 2006).

1.3.1 Life cycle assessment (LCA)

The life cycle thinking concept, i.e., the concept of exploring the life cycle of a product, dates back to the 1950's and 1960's, mainly focused on the life cycle costs for public purchasing (Curran, 2012). The application of this concept into environmental analysis of products dates back to the 1970's, when the first LCA studies were performed. During the 1990's the LCA methodology started to be harmonized, through a remarkable growth of scientific and coordination activities worldwide (e.g. the appearance of the first scientific papers) (Guinée et al., 2011).

LCA is standardized by the ISO 14040 and 14044 (ISO, 2006a, b), which divides the methodology in four phases: (1) Goal and scope definition; (2) Inventory analysis; (3) Impact assessment; and (4) Interpretation. Even though the proposed procedure follows the order previously mentioned, these four phases are highly interactive, i.e., the LCA practitioner has the freedom to move back to the goal and scope definition after a preliminary inventory work, to skip to the interpretation phase in the beginning of the study, etc, as represented in Figure 1.5 (Curran, 2012).

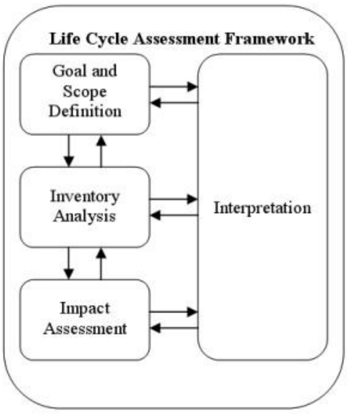

Figure 1.5: The general methodological framework for LCA (extracted from ISO (2006a))

It is in the first stage of the study where the goal and the scope are defined. The goal should state the intended application, the reasons to carry out the study, the intended audience, and whether the results are to be used in comparative assertions disclosed to the public. The scope definition includes several detailed aspects of the study, as the system boundaries, the impact categories, definition of the functional unit, etc. (Curran, 2012; ISO, 2006a, b).

The inventory analysis involves the quantification of relevant inputs and outputs of a product system, through data collection and calculation procedures (ISO, 2006a). Different methods for Life Cycle Inventory (LCI) can be found in literature, for instance process-based, input-output based, and hybrid methods (Suh and Huppes, 2005). The data collection for a product system may be very exhaustive, so LCA studies usually split data collection into foreground and background data. The former refers to the data that shall be directly collected during the LCA study, either through primary data (i.e., collected by the LCA analyst) or through secondary data (i.e., from literature). Background data refers to LCI databases, such as ecoinvent database (www.ecoinvent.ch), ELCD database (http://lca.jrc.ec.europa.eu/), USLCI database (http://www.nrel.gov/lci/), among others, which have a significant contribution in the growth of LCA studies.

An important issue at the inventory analysis is allocation, which is a procedure to partition the inputs and/or output flows of a process between one or more products that are being produced in that process. Several allocation methods can be found in literature, but no standard method has been developed. Usually, environmental standards (at continent or country levels) adopt the suggestion from ISO 14044, which proposes the LCA analyst to choose an allocation method based on the following procedure: (1) Avoid allocation, by splitting the process in sub-processes or by system expansion; (2) when this is not possible, to use allocation based on physical relationships (e.g. mass, energy); and finally (3) allocate using other relationships (e.g. economic value of the products) (ISO, 2006b).

In the third phase, commonly called as Life Cycle Impact Assessment (LCIA), the environmental impacts of the product system are evaluated, based on the results obtained from the LCI. The procedures to transform the results of the LCI into the LCIA are called classification, characterization (both mandatory), normalization, grouping, and weighting (the last three are optional) (ISO, 2006b). Several LCIA methods and methodologies (European Commission, 2011b) have been created in the last years, for instance the Recipe methodology (Goedkoop et al., 2009). LCIA methods make use of indicators to represent the magnitude of the environmental impact, and they can be classified into two types: Midpoint and Endpoint. Midpoint indicators represent a step in the cause-and-effect chain of a particular impact category (e.g. acidification potential), while endpoint indicators represent the end of the cause-effect chain at specific areas of protection[*] (AoP) (e.g. damage to human health) (Bare et al., 2000), as it can be visualized in Figure 1.6. Through their International Reference Life Cycle Data System (ILCD) Handbook, the European Commission recommended different midpoint and endpoint LCIA methods for eleven environmental impact categories, e.g. the USEtox method was recommended for freshwater ecotoxicity at midpoint level (European Commission, 2011b; Hauschild et al., 2013).

It is in the last phase of LCA, so-called interpretation, when an evaluation of the results from the LCI and/or the LCIA is made in relation to the goal and scope defined. This evaluation can include the identification of significant issues, sensitivity analysis, limitations of the study, etc (Curran, 2012; ISO, 2006a, b).

[*] Areas of protection can be defined as the society's understanding of the final effect of certain environmental interferences, and in LCA are usually classified in human health, ecosystems, and resources

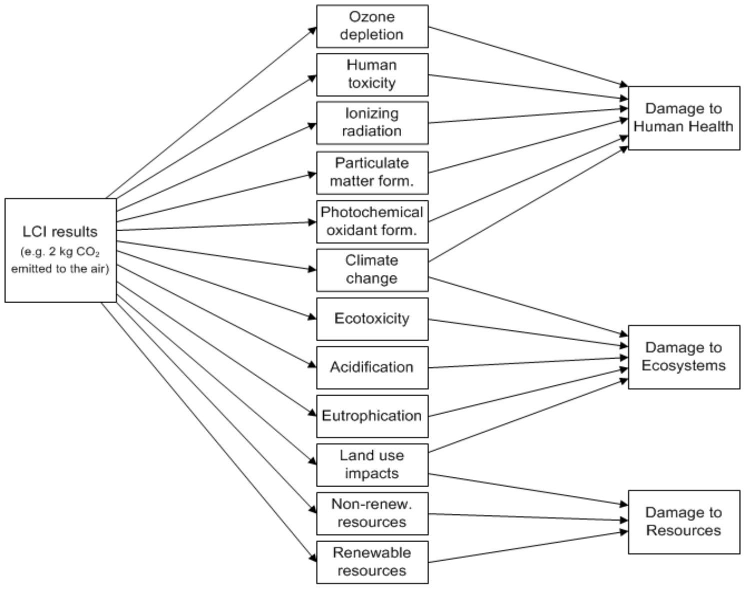

Figure 1.6: Relationship between the LCI (left), midpoint indicators (middle), and endpoint indicators (right)

There are two approaches to make a LCA, named attributional and consequential (Finnveden et al., 2009). The former focuses on describing relevant physical flows to and from a product's life cycle, while the latter aims to describe how these flows shall change in response to possible decisions. Several methodological differences exist between these two approaches, for instance in attributional LCA average data is used (e.g. average electricity mix from a country), while in consequential LCA the marginal data should be used, i.e., the data that will be directly affected by a certain change (e.g. even though most Norwegian electricity is produced from hydropower, a small increase in electricity demand will result in an increase in fossil-based electricity production due to technical and economic constraints (Earles and Halog, 2011)). While the attributional LCA focuses on the system boundaries of the product studied, the consequential LCA goes further, allowing the inclusion of iLUC in the study (Guinée et al., 2011; Sanchez et al., 2012).

1.3.2 Resource accounting methodologies[†]

LCA is one of the most used methodologies to assess the environmental sustainability of products. Nevertheless, it has some disadvantages, such as the large amount of data required, giving opportunity to the use of other types of methodologies that still consider the life cycle perspective but are mainly resource-based (e.g. energy accounting) (Huijbregts et al., 2006).

[†] Partly extracted from Swart, P., Alvarenga, R.A.F., Dewulf, J., 2014. Abiotic resource use, in: Hauschild, M., Huijbregts M.A.J. (Eds.), Encyclopedia of LCA, Volume IV: Life Cycle Impact Assessment. Springer press (submitted).

Because these methodologies are applied to products and take into account a life cycle perspective, they are often considered as LCIA methods (Alvarenga et al., 2012). Nevertheless, in this PhD dissertation hereafter they will be called as resource accounting methodologies (RAM).

RAM are able to provide results on the environmental sustainability of a product due to the philosophy of '*less is better'*. They generally sum up all the resources consumed/used in the life cycle of a product. In order to provide results in single score indicators, the resources are usually represented in common units (e.g. MJ), otherwise the same information as given by the LCI would be obtained.

1.3.2.1 Energy

Accounting for energy use is a concept that was introduced in the 1970s (Boustead and Hancock, 1979; Pimentel et al., 1973), and standardized by VDI (1997). Energy-based RAM account for the energy extracted from the natural environment (i.e. the cradle) to support the technosphere system. They account not only for types of energy but also for materials, by quantifying their energy content. These methodologies have been made operational as LCIA methods for LCA, for instance as the Cumulative Energy Demand (CED) for the ecoinvent database (Ecoinvent, 2010; Hischier et al., 2009) and as the Primary Energy Demand (PED) for the Gabi database (PE International, 2012). In principle, CED and PED are the same, only differing in names and compatibility to databases and/or software.

Fossil energy consumption (one category of the CED and the PED) can be a useful screening tool (Huijbregts et al., 2010; Huijbregts et al., 2006) and is able to provide consistent results when LCA studies are interested in information solely regarding the consumption of fossil fuels during the product's life cycle. It is also common to find energy-based RAM in some traditional midpoint LCIA methods, i.e., the energy content of fossil fuels is used as characterization factor (e.g., the category 'Fossil depletion' of the method Recipe Midpoint (Goedkoop et al., 2009)).

1.3.2.2 Exergy

By definition, the exergy of a resource or a system is the maximum amount of useful work that can be obtained from it (Dewulf et al., 2008). Exergy analysis is usually used in industry to analyze the (in)efficiencies of processes. The cumulative exergy consumption (CExC), introduced by Szargut et al. (1988), is the exergy of the overall natural resources consumed in the life cycle of a product. Exergy-based RAM have been made operational as LCIA methods for LCA through different LCI modeling approaches. For the process-based ecoinvent database, the Cumulative Exergy Demand (CExD) was operationalized in Bösch et al. (2007) and the Cumulative Exergy Extraction of the Natural Environment (CEENE) was operationalized in Dewulf et al. (2007). The latter was recommended as the most appropriate thermodynamic indicator for resource use accounting in Liao et al. (2012b). These two operational methods have some differences, including the approach to account for metals and minerals, but also the approach to account for biotic resources: While the exergy of the biomass is accounted in the CExD, in the CEENE the exergy deprived from nature due to land use is accounted. For the economic input-output U.S. 1997 database, the Industrial Cumulative Exergy Consumption (ICEC) is operationalized in Zhang et al. (2010a).

1.3.2.3 Emergy and similar methodologies

Introduced by Odum (1996), emergy accounts for the total available energy used to make a product. In contrast to other RAM (e.g. exergy-based), which usually set the natural environment as 'cradle', emergy has a different system boundary. The natural environment is part of the system, and the 'cradle' is considered to be the energy forces outside of the Earth's crust physical limits, e.g. the sun (Liao et al., 2012a) (Figure 1.7). Emergy considers tidal, geothermal and solar energies as main energy sources that rule life on Earth, and the latter is taken as reference for its unit (Joules of solar energy – J_{se}). Emergy has received several criticisms (e.g. allocation rules) and some propositions to overcome them, together with challenges to implement emergy into LCA, have been suggested in literature (Ingwersen, 2011; Rugani and Benetto, 2012).

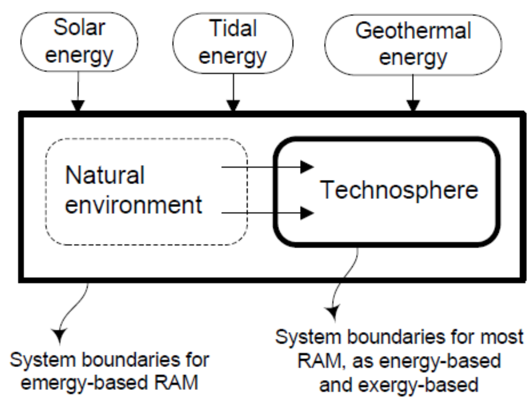

Figure 1.7: Simplified scheme representing different system boundaries considered in RAM

Due to the limited acceptance in the scientific community, Hau and Bakshi (2004a) developed the ecological cumulative exergy consumption (ECEC). According to the authors, it overcomes some weaknesses of emergy. But if identical system boundaries, allocation and quantification methods are used, emergy and ECEC should produce equivalent results. The ECEC has been made operational as LCIA method for the economic input-output U.S. 1997 database in Zhang et al. (2010a). It accounts for several ecosystem services as well and is commonly used in complementation to the industrial ICEC (Baral and Bakshi, 2010; Baral et al., 2012; Urban and Bakshi, 2009; Zhang et al., 2010a).

Using emergy as starting point, the Solar Energy Demand (SED) accounts for the amount of solar energy needed to produce a certain product. It is an emergy-based method that was made operational as LCIA method for LCA to the ecoinvent database (Rugani et al., 2011). According to the authors it shares the same conceptual rationale as emergy, but they do not use the same approach for allocation. Moreover, unlike emergy, the SED does not account for human labor and most of the ecosystem services (MEA, 2005): it accounts for provisioning services only.

1.3.2.4 Ecological Footprint

Developed by Wackernagel and Rees (1996) and further enhanced by the Global Footprint Network (2009) and Ewing et al. (2010), the Ecological Footprint is defined as the ecological surface area needed to sustain a certain system. When applied to products, the requirement of area to produce the raw materials and to absorb CO_2 emissions is calculated, in units of land use (e.g.: m^2.year). It has been made operational as LCIA method for LCA through the ecoinvent database (Huijbregts et al., 2008). In this methodology, solely direct land use, nuclear energy, and fossil energy (indirectly through the fossil CO_2 emissions) are accounted. Nevertheless, it has a strong appeal to society, since it can directly be compared with the Earth's carrying capacity (represented through the actual land availability), and as a consequence it has an easy communication capability with stakeholders (due to its unit).

1.3.2.5 Human appropriation of net primary production (HANPP)

The human appropriation of net primary production (HANPP) is a socio-ecological indicator of land use intensity, measuring the human domination of the biosphere (Erb et al., 2009; Haberl et al., 2007). It makes use of net primary production (NPP), which is defined as the amount of biomass produced by green plants through photosynthesis per unit of time and area

(Erb et al., 2009). In the HANPP indicator, the NPP of the potential natural vegetation (NPP_{pot}) is compared with the NPP of the actual vegetation (NPP_{act}), obtaining the NPP lost due to human-induced changes in the ecosystem productivity, called ΔNPP_{LC}. The NPP_{act} can be split into NPP harvested (NPP_h) and the remaining NPP (NPP_t). In this way, the HANPP is calculated by subtracting the NPP_{pot} by the NPP_t or by summing the ΔNPP_{LC} with the NPP_h (Erb et al., 2009; Haberl et al., 2007), as shown in Figure 1.8.

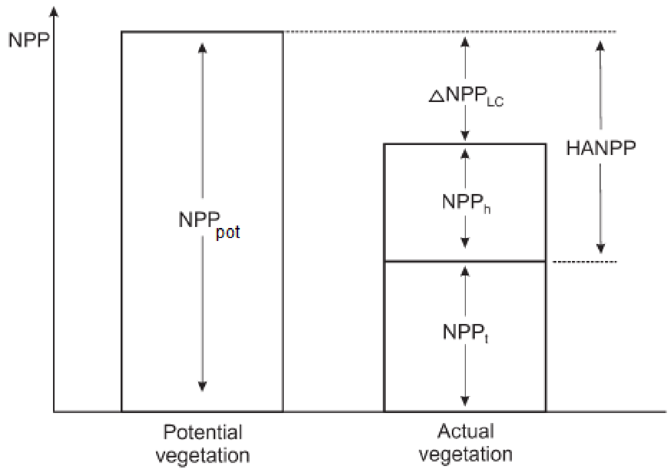

Figure 1.8: Representation of the HANPP indicator, which involves the potential NPP of natural vegetation (NPP_{pot}), the harvest fraction of the actual NPP (NPP_h), the remaining NPP (NPP_t), and the difference between actual and potential NPP (ΔNPP_{LC}) (extracted from Erb et al. (2009))

The HANPP indicator is used mainly for land use assessment, and cannot be consistently applied to products. However, its partial indicators (e.g. NPP_{pot}) have the potential to be used in environmental impact assessment of biobased products, as will be demonstrated in the next chapters.

1.4 EVALUATION OF LAND USE AND LAND USE IMPACTS THROUGH ENVIRONMENTAL SUSTAINABILITY ASSESSMENT METHODOLOGIES

As mentioned before, the proper evaluation of land use and land use impacts is fundamental if we take into account the raise of a biobased economy, where an increase pressure on land is likely. Therefore, in this section we made a critical analysis on this topic in the aforementioned methodologies.

1.4.1 Land use impacts in LCA

Land use impacts are poorly considered in LCA, mainly for two reasons:

- Due to the historical backgrounds of LCA, i.e. it was predominantly used for fossil-based industrialized products (e.g. plastics and machinery). As a consequence, most LCIA methodologies were mainly focused on emission-related environmental impacts, overlooking land use impacts in LCA studies;
- Most LCIA methods are currently site-generic, i.e., the environmental effects of emissions and/or resource extractions are not specific to the area where they are actually occurring. This can have a huge influence in the results, especially for some environmental impact categories, as eutrophication and acidification, but also for land use impacts. This is actually a challenge in the LCA community, i.e., the spatial-differentiation of LCIA methods (Hauschild, 2006).

Nevertheless, the LCA community is aware of the importance of land use impacts, and several efforts have been done to improve its evaluation in LCA. For instance, the increase on research projects between Universities and research institutes dealing with this topic, as the LC-Impact project (http://www.lc-impact.eu/wp1-resource-use-impacts) and the UNEP/SETAC project called "Operational Characterization Factors for Land use Impacts on Biodiversity and Ecosystem Services".

Several land use impacts should be considered in a LCA study. According to Milà i Canals et al. (2007a), apart from those land use impacts that are already considered in traditional LCIA methodologies (e.g. biotic resource depletion from extraction of wood from natural forests or toxicity and ecotoxicity through the application of pesticides), the environmental impacts on ecological functions of land should be covered, such as:

- Impacts on the existence value of biodiversity, which is a key element on the AoP natural environment. Several LCIA methods have been developed so far, but just a few are site-specific. Examples of site-generic LCIA methods dealing with biodiversity are Müller-Wenk (1998), Goedkoop and Spriensma (2000), Weidema and Lindeijer (2001), and Vogtlander et al. (2004); while examples of site-specific LCIA methods dealing with biodiversity are Michelsen (2008) for Norway, Schmidt (2008) for Denmark, Malaysia, and Indonesia, and de Baan et al. (2012), on a global scale;

- Impacts on the biotic production potential, i.e., impacts that are affecting the potential productivity of biomass from land, as the decrease of soil fertility. The method from Brandão and Mila i Canals (2012) is an example of an operational site-specific (on a global scale) LCIA method for impacts on the biotic production potential.
- Impacts on the ecological soil quality and other life support functions of the soil, as carbon cycling. Examples of LCIA methods are Núñez et al. (2012), dealing with soil erosion on a global scale, and Saad et al. (2011), dealing with erosion resistance, groundwater recharge, and mechanical and physicochemical filtration, for Canada. The methods from Baitz et al. (2000) and Beck et al. (2010), dealing with several ecological functions of soil, and Milà i Canals et al. (2007b) have site-generic indicators that can be considered as dealing with impacts on both soil ecological functions and the biotic production potential.

There are also other LCIA methods that attempt to evaluate land use impacts through other approaches, as Wagendorp et al. (2006), which evaluates land use impacts through ecosystem thermodynamics.

Even though several examples of LCIA methods dealing with land use impacts could be raised, just a few of them are site-specific and/or easily available for LCA users, i.e., in an operational LCIA method. Future challenges for land use impacts and LCA are the creation of spatial-differentiated characterization factors that can be set in an operational way for LCIA methods (Koellner et al., 2012). The use of geographic information systems (GIS) has a big potential for that goal (Geyer et al., 2010).

1.4.2 Accounting for land use in RAM

Certain RAM, as energy, exergy, and emergy, are not able to consider the environmental impacts from land use and LUC (e.g. biodiversity loss); in the same way they are not able to quantify other types of environmental impacts (e.g. climate change). Nevertheless, they are still able to account for it as a resource used during the life cycle of a product.

Accounting for land use in RAM can be delicate, as double-counting with biomass is possible. For instance, in exergy-based RAM the land use can be accounted by the solar exergy, but biomass also represent part of this solar exergy, thus if both land use and biomass are accounted it will cause double-counting (Dewulf et al., 2007). In order to avoid that, RAM usually have to choose only one way of accounting: (1) accounting for the biomass content; or (2) accounting for the land use/occupation. Due to these characteristics, land use/occupation and biomass may be called as *land resources*.

In energy-based RAM, as the operational LCIA methods CED and PED, land resources are accounted indirectly through the energy content of the (produced) biomass. This methodological approach results in two weaknesses. First, agricultural systems with higher yields do not show better results even though they require less land occupation for the same amount of biomass production. Second, because these methods account for the energy content of the biomass harvested, which is produced at agricultural (or forestry) systems, it can be considered that the system boundary of the method does not actually reach the line between natural environment and technosphere, as those systems usually are not considered to be from the former (check Liao et al. (2012a) for more details about systems boundaries of LCIA methods).

In exergy-based RAM, two approaches for land resource accounting can be found. In the operational LCIA method called CExD, the exergy content of the biomass is accounted (as in energy for the CED). Therefore, the same limitations are found, i.e., the efficiency of land use is overlooked and its system boundary might not correspond to the border between natural environment and technosphere for biomass. The CEENE method, another RAM set operational as LCIA method, accounts for the use/occupation of land as land resources, through the quantity of photosynthetically active solar exergy deprived from nature due to land use. This procedure allows accounting not only for land use for biotic resources, but also for other purposes (e.g. built-up land). However, the method is not site-specific and, by choosing to account for land occupation, land resources from natural systems which had no human interference (therefore no land use) during biomass growth (e.g. wood from natural forests) might not be accounted.

The emergy-based RAM named SED, which is also set operational as LCIA method, follows the same approach as the CEENE method, but instead of accounting for the quantity of photosynthetically active solar exergy deprived from nature due to land use, it accounts for the total *empower density of the Earth*[‡] divided by the terrestrial land area of the Earth. This approach may be criticized for creating an averaged site-generic characterization factor, i.e.,

[‡] According to Odum (1996), the *empower density of the Earth* is the total emergy that is entering the Earth boundaries, per unit of time (e.g. GJ_{se}/year)

land resources are considered to be receiving the same amount of solar emergy despite their location in the globe, which does not represent reality.

In the ecological footprint, land resources are accounted by the land use, i.e., basically the area and time needed to produce the biomass. On the other hand, emissions of CO_2 are accounted and transformed into equivalents of land use, in order to have a final indicator in the same unit (m^2.year). Because several assumptions are made to allow those transformations (e.g. assuming a carbon uptake factor of 0.4 kg CO_2/m^2.year) and because other resources are usually not accounted (e.g. metals), this RAM has some limitations to be used to assess the environmental sustainability of products.

The approach for accounting for land resources in the HANPP is interesting because it compares the actual biomass production with the potential natural biomass production that would occur in the same area. However, because this indicator is focused on biotic resource accounting, it does not account for abiotic resources that were used for the production of the actual biomass (e.g. fertilizers and diesel).

1.5 OBJECTIVES AND STRUCTURE OF THE PHD DISSERTATION

The objective of this PhD dissertation is characterized by two main research issues. The first, which is more methodological, regards on how to make proper environmental sustainability assessment of biobased products in terms of resource demand. The second, applied to case studies, brings the discussion about the environmental sustainability of biobased products themselves, in particular whether they are more environmentally sustainable than their fossil-based references.

As it was pointed out in the previous sections, several gaps exist in the evaluation of natural resources and in particular land use and land use impacts in environmental sustainability methodologies. Considering the case of exergy-based RAM, the current methodologies that are operational as LCIA methods are not able to create a fair comparison between fossil-based and biobased products, since either land use is not accounted (CExD) or it is accounted without spatial-differentiation (CEENE). This is the first research question of this PhD Dissertation, and it is answered in Chapter 2, where a new exergy-based spatial-differentiated LCIA method is proposed for land resource accounting.

Land availability is already an important issue nowadays, and in a more biobased economy it will be critical. Currently, RAM are not truly able to evaluate if a man-made (agricultural or forestry) system is producing more products than it is consuming natural resources, as done by the HANPP indicator (but solely for biotic resources in the latter). How to evaluate that through a RAM that takes all physical natural resources into account, i.e., land next to fossils, is the second research question of the PhD, and it is answered in Chapter 3, where a new indicator is proposed to evaluate the overall natural resource balance of man-made systems through exergy. Chapters 2 and 3 are related to the methodological research issue of this PhD Dissertation.

Even though a biobased economy appears to be a sustainable path for our society, the term 'biobased product' does not mean automatically environmentally sustainable products. Indeed, are biobased products more environmentally sustainable than their fossil-based references? The answer to this question may vary depending on the product considered, the environmental sustainability methodology used, and even the variety of environmental impact categories considered (e.g. acidification, eutrophication, climate change, etc). In Chapter 4 and 5 we answered this research question specifically for bioethanol-based PVC, through attributional and consequential LCA, respectively, and using 14 environmental impact categories.

Taking into account the environmental gains that biobased products usually have over their fossil-based references, i.e., lower climate change and fossil depletion impacts, if more than one final use for intermediate biobased products is possible, which one would bring more environmental gains? For instance, is it better to use bioethanol as fuel or as feedstock for plastics? This specific case for bioethanol is answered in Chapter 6, considering the current reality of Brazil. Chapters 4, 5, and 6 are related to the applied research issue of this PhD Dissertation.

CHAPTER 2: Exergy-based accounting for land as a natural resource in life cycle assessment[§]

ABSTRACT

In Life Cycle Assessment (LCA), literature suggests accounting for land as a resource either by what it delivers (e.g. biomass content) or the time and space needed to produce biomass (land occupation), in order to avoid double-counting. This paper proposes and implements a new framework to calculate exergy-based spatial explicit characterization factors (CF) for land as a resource, which deals with both biomass and area occupied on the global scale. We created a schematic overview of the Earth, dividing it into two systems (human-made and natural), making it possible to account for what is actually extracted from nature, i.e., the biomass content was set as the elementary flow to be accounted at natural systems and the land occupation (through the potential natural net primary production) was set as the elementary flow at human-made systems. Through exergy, we were able to create CF for land resources for these two different systems. The relevancy of the new CF was tested for a number of biobased products. Site-generic CF were created for land as a resource for natural systems providing goods to humans, and site-generic and site-dependent CF (at grid, region, country, and continent level) were created for land as a resource within human-made systems. This framework differed from other methods in the sense of accounting for both land occupation and biomass content, but without double-counting. It is set operationally for LCA and able to account for land resources with more completeness, allowing spatial differentiation. When site-dependent CF were considered for land resources, the overall resource consumption of certain products increased up to 77% in comparison with site-generic CF based data. This paper clearly distinguished the origin of the resource (natural or human-made systems), allowing consistent accounting for land as a resource. Site-dependent CF for human-made systems allowed spatial differentiation, which was not considered in other resource accounting life cycle impact assessment (LCIA) methods.

Keywords: LCA, exergy, land, resource, biomass, NPP

[§] Redrafted from: Alvarenga, R.A.F; Dewulf, J.; Van Langenhove, H.; Huijbregts, M.A.J. 2013. Exergy-based accounting for land as a natural resource in life cycle assessment. *The International Journal of Life Cycle Assessment*, v.18, pp 939-947.

2.1 INTRODUCTION

With the World's population projected to grow from 6.9 billion in 2010 to more than 9 billion in 2050 (United Nations, 2009) associated with a growth rate of 5% of the Human Development Index from 1980 to 2010 (United Nations, 2010), the consumption of overall Earth resources is expected to rise. Due to the depletion of non-renewable resources and policy actions to mitigate climate change, an increase pressure on land as a resource is to be expected (Bessou et al., 2011; Easterling and Apps, 2005). Land use addresses several environmental impacts and can affect the ecosystem services (MEA, 2005). Much effort is being done by the scientific community in order to consider these consequences on the environment when using Life Cycle Assessment (LCA) methodology (de Baan et al., 2012; Milà i Canals et al., 2007a; Wagendorp et al., 2006; Zhang et al., 2010a; Zhang et al., 2010b). With respect to the provisioning services (one category of ecosystem services), humans harvest the natural resources, e.g. wood and metals, or they fully occupy the land for productive or non-productive uses, e.g. agriculture and urbanization, respectively.

When accounting for the cumulative resource consumption of a certain product through LCA, provisioning services from land, which hereafter will be called as *land resources*, can be quantified through several approaches that may be divided in two groups (Liao et al., 2012b). The first group of approaches considers the Earth as a closed system, and includes the ecological processes that induce the resource production, with solar, geothermal, and tidal energies as major energy inputs. In this group, the *cradle* (ISO, 2006b) may be defined as the Sun. Emergy analysis (Odum, 1996), the Ecological Cumulative Exergy Analysis (Hau and Bakshi, 2004b), and the Solar Energy Demand (Rugani et al., 2011) are examples of approaches from this first group. The second group considers only what is delivered by nature to humans, i.e., they limit their system boundaries to the border between ecosphere and technosphere. In other words, the *cradle* is the natural environment. This last group of approaches is often used in LCA as life cycle impact assessment (LCIA) method, and is usually considered as a midpoint indicator in the impact pathway of resource depletion (European Commission, 2011b; Liao et al., 2012b). Regarding land resources, there are basically two ways for accounting: (a) by the content of the biomass harvested, e.g., Cumulative Energy Demand (CED) (Hischier et al., 2009) and Cumulative Exergy Demand (CExD) (Bösch et al., 2007); and (b) by the area and time needed to produce the biomass (land occupation), e.g., Cumulative Exergy Extraction from the Natural Environment

(CEENE) (Dewulf et al., 2007). These methods account for the overall cumulative resource consumption of a product during its life cycle (fossils, water, metals, land, etc.). Specifically for land resources, they needed to choose one way of accounting in order to avoid double-counting, i.e., to keep away from accounting land resources twice. It is also common that some other LCIA methods use the occupation of areas (which is expressed by a *land occupation* elementary flow) to assess impacts on biodiversity on an endpoint level (Bare et al., 2000; Finnveden et al., 2009), and results on midpoint level are provided as well (Goedkoop et al., 2009; Guinée et al., 2002; Jolliet et al., 2003). In these cases land occupation is accounted, but it is not explicitly considered as a natural resource. Furthermore, even though it is known that the environmental impacts of a product, along its life cycle, may happen at many different locations of the world, most of the LCIA methods neglect this spatial variation. This differentiation is relevant for all non-global impact categories, including land resources (Finnveden et al., 2009; Hauschild, 2006).

This paper proposes and implements a new framework to calculate exergy-based spatial explicit characterization factors (CF) for land resources in LCA, limiting the cradle to the border between ecosphere and technosphere, and dealing both with biomass and area occupation on the global scale. Exergy is used as indicator due to its scientific concept, that comes from the Second Law of Thermodynamics, which is ruling ecosystems and which reflects the physical and chemical potential and usefulness of resources (Dewulf et al., 2008), and due to its completeness for resource use accounting (Liao et al., 2012b). Also, because other natural resources (e.g. fossil fuels) can be expressed in the same unit, it provides a straightforward resource accounting method and allows all resources to be aggregated into a single score (Bösch et al., 2007; Dewulf et al., 2007). Exergy has several uses in environmental science and technology (Dewulf et al., 2008), but it is important to make clear that the use of exergy in this paper is focused on the cumulative resource accounting perspective (and specific for land resources). The CF calculated in this paper ought to be integrated into overall resource exergy-based methods, as the CExD and the CEENE. The relevancy of the new CF is tested for a number of biobased products.

2.2 MATERIALS AND METHODS

2.2.1 Framework

For the approaches that set the cradle to the natural environment, it is important to make a clear definition of where the frontier between ecosphere and technosphere is located, through naturalness levels. The most straightforward way is to divide in two levels: Natural and Human-made systems. Figure 2.1 presents this approach, which was used as starting point for our framework. This enabled us to account for the land resources that were deprived from the natural environment, in order to deliver products for humans. It is important to mention that this system classification regards exclusively to the origin of the resources.

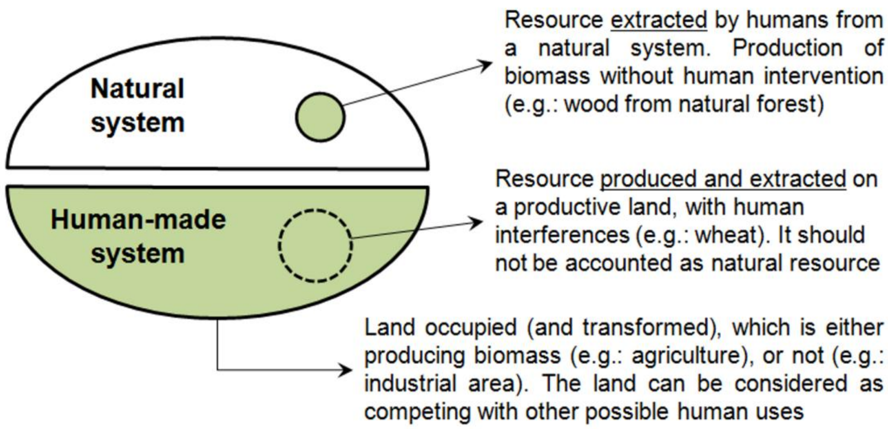

Figure 2.1: Schematic representation of land resources from two different systems, regarding their origin

The approach for accounting non-renewable resources consumed (e.g. crude oil) using exergy-based LCIA methods (CExD and CEENE) is through their exergy content, since this is the exergy that is deprived from nature. We understand the same approach should be used for renewable resources originated from natural systems, given that these resources were produced exclusively by nature, i.e., negligible human intervention happened prior to the extraction of the biomass. In other words, a system can be qualified as natural if the production of its biomass can be maintained with no or negligible human intervention. Human intervention typically means the introduction of operations relying on natural resources from elsewhere (e.g. ploughing and fertilization). Examples of land resources from natural systems are wood harvested from primary forests, seafood from non-modified ocean waters, and grass consumed in extensive pasture lands. Therefore, the land resources from natural systems were set in this paper to be accounted through the exergy content of the biomass extracted. More detailed information about four forest types considered by the authors as natural systems can be found in the Supporting Information (S1).

In human-made systems, the land area has been previously transformed from natural to human-made environment, and is being occupied either for non-productive land use (e.g., urbanization), or for a productive land use, with significant human intervention at the production, as agriculture, livestock (intensive pasture), intensive wood production (in forest plantations), fish cultivation (in aquaculture), etc. In these productive land uses, we understand that the actual biomass yield is considered not to be extracted from nature, but produced within a human-made system (technosphere); for the authors of this paper, what is actually deprived from the natural environment and/or from other human uses is the land area, next to other natural resources brought to the specific human-made system (e.g. fossil fuels, water, etc). For this reason, in specific human-made systems the land occupation was set to be accounted for as land resource competing with other possible human uses. More detailed information on a forest type considered by the authors as human-made system can be found in the Supporting Information (S1).

Unlike natural systems, where the biomass content is directly expressed in terms of exergy, land occupation by human-made systems cannot. In Brehmer et al. (2008) and in the CEENE method (Dewulf et al., 2007), the solar irradiation available for photosynthesis is used as a proxy for land occupation, since this solar exergy is no longer available to nature. However, the photosynthetic solar exergy may not be a consistent indicator for the resource value of land (especially when spatial-differentiation is sought), since other factors are not taken into account, such as climate and soil quality. The natural potential Net Primary Production (NPP), which is the amount of NPP a land area would produce if it was not occupied by humans (Erb et al., 2009; Haberl et al., 2007), can be used as a better proxy to represent the resource value of land. It considers several local natural conditions, such as solar exergy, soil quality, water availability, temperature, among others, allowing spatial-differentiation in a consistent way. In this sense, the potential NPP is a more representative base to quantify land for specific human-made systems in exergy terms.

2.2.2 Characterization factors

In order to make impact assessment methods operational for LCA, the elementary flows that ought to be used in the Life Cycle Inventory (LCI) (e.g. emission of CO_2) need to receive a value representing the degree of its impact on the environment, so called Characterization Factors (CF) (ISO, 2006b).

Starting from the framework set in Figure 2.1, CF of land resources from natural systems were derived from the content of the biomass extracted from the land. We considered the chemical exergy value (CEV) of the biomass in subject to express the exergy content, which can be calculated through several methods (Szargut et al., 1988). According to Vries (1999) it is preferable to consider the group contribution method, since it is more accurate than the β - Low Heating Value (LHV) method and others. In LCI databases, the biomass characteristics are typically expressed by their amount harvested (kg or m^3) and/or their energy content, which is usually the High Heating Value (HHV). Therefore, CF shall be calculated through correlations between the biomass' CEV (MJ_{ex}) and its HHV (MJ) or quantity (kg or m^3). Since the water content in biomass can differ considerably between species, we prefer to make a ratio between CEV and HHV where possible, in order to generate the CF for natural systems (equation 2.1):

$$CF_{natural} = {}^{CEV\ (MJ_{ex})}\!\big/_{HHV\ (MJ)} \qquad (2.1)$$

For land resource CF in human-made systems, we set to account for the land occupation, based on potential NPP. As source of data, we used Haberl et al. (2007), allowing the generation of site-generic and site-dependent $CF_{human\text{-}made}$ (at continent, country, region, and grid level). NPP in Haberl et al. (2007) is represented in mass of carbon (kgC), and to transform it into exergy units, we calculated biomass-exergy conversion factors (MJ_{ex}/kgC) for specific natural vegetations. First, the Earth's land was divided into different biomes. We used thirteen of the fourteen biomes from Olson et al. (2001) excluding mangroves, since it is a biome that mixes water and land surfaces. Then, we partitioned the biomes' NPP into above and belowground biomass. For tundra, we used the data from Shaver and Chapin (1991) and for desert and grasslands (5 different types) we used the data from Hui and Jackson (2006). For forests biomes, we divided the NPP into roots, woods, and leaves, by using the data from Luyssaert et al. (2007). To obtain the chemical composition of the biomes' vegetation with its typical species, we used the Phyllis database (Phyllis, 2011), except for data on grass roots, where we used data from Saunders et al. (2006). We proceeded with the exergy calculations, applying the group contribution method or the β-LHV method. More information on the calculations can be found in the Supporting Information (S2). As a result we obtained conversion factors for each of the thirteen biomes, and further on, we calculated a single average. Then, we multiplied the value of each pixel from the map from Haberl et al. (2007) by the appropriate conversion factor (equation 2.2).

$$CF_{human-made} = Potential\ NPP\ (kgC/m^2a) \times Conversion\ factor\ (MJ_{ex}/kgC) \qquad (2.2)$$

In the map generated, each pixel had a specific average value for potential NPP (MJ_{ex}/m^2.year/pixel), which is the site-dependent CF at grid level. Since the map was drawn through equidistant cylindrical projection, the area of a pixel on the map gets higher than it is in reality when moving towards the poles. Because of that, average values for specific regions may not be representative for large areas. Therefore, to draw the site-dependent CF (at region, country, and continent level) we multiplied the potential NPP value of each pixel by its real surface area, then we summed these values within the region we intended to have CF, and divided it by the sum of the real surface areas of the pixels from the same region, generating area-weighted average values.

2.2.3 Practical implementation

We implemented the CF produced in this paper into practical conditions, divided in two levels. First, on a CF level, we intended to check the framework and the CF produced, in comparison to other LCIA methods that account for land resources by the same system boundaries. Then, on an overall resource footprint level, we intended to check the share of land resources in products from existing LCI databases, and the effects of regionalization on final results. These practical implementations were done through case studies.

For the first level we applied the CF (from human-made and natural systems) into a case study of wood production systems, in which data for land resources were based on processes from ecoinvent database v2.2 (Ecoinvent, 2010).The functional unit was the production of 1 m^3 of wood (at forest road). For natural systems, we considered the production of Meranti and Azobe woods in Malaysia and Cameroon respectively (Althaus et al., 2007). For human-made systems, we selected the production of Eucalyptus in Thailand and Parana Pine in Brazil (Althaus et al., 2007). Then, we compared the results with other LCIA methods: CED, CExD, and CEENE. More information on the LCI of the land resources consumed in this case study, based on the ecoinvent database, can be found in the Supporting Information (S3). This wood production case study was applied with the purpose of illustrating the differences on accounting for land resources in human-made and natural systems, by different LCIA methods, and was named “Case study 1”.

For the second level, first we implemented the CF into ecoinvent database elementary flows, although we were able to apply only the site-generic CF, since this LCI database does not support (yet) site-dependent CF. After that, we included these CF in the elementary flows from *Land Occupation (and transformation)* category and the biotic portion of the *Renewable Resources* category in the CEENE method. For all other natural resources (fossil fuels, water, metals, and minerals) we relied on the original CF from the CEENE method. Then, we applied this customized CEENE method into a case study of human-made biomass products, using 9 biomass production processes from ecoinvent database v2.2 (the name of the processes can be seen in Supporting Information – S4), and summed up all natural resources with the same unit, as done in the original CEENE method. Besides the site-generic CF, we also applied site-dependent CF (at continent, country, and regional level) for the direct land occupation. With this case study, named “Case study 2”, we could evaluate the share of land resources in comparison to the overall natural resource footprint and how spatial differentiation on land resources can affect the final result of an overall resource-based LCIA method.

2.3 RESULTS AND DISCUSSION

2.3.1 Characterization factors

2.3.1.1 CF of land resources in natural systems

Given that land resources from natural systems are quantified by the exergy content of the biomass harvested, site-generic $CF_{natural}$ were based on calculations by Dewulf et al. (2007), where the exergy/energy ratios had less than 2% difference among species, with a final average value equal to 1.06 MJ_{ex}/MJ.

2.3.1.2 CF of land resources in human-made systems

$CF_{human\text{-}made}$ were obtained from the land occupation, based on potential natural NPP. We obtained a biomass- exergy conversion factor of 42.9 MJ_{ex}/kgC, which is the average value of the thirteen biomes’ conversion factor, with a coefficient of variance of 0.02. Then, we multiplied the values of the potential NPP map by the biomass-exergy conversion factor. As a result, we obtained a map with potential NPP in exergy units, with a grid size of 5' geographical resolution (approximately 10 km × 10 km at the equator), that was used to generate the $CF_{human\text{-}made}$ (Figure 2.2). Figures of maps with larger scales can be found in the Supporting Information (S5). The ASCII file of this map can be downloaded from the link in the Supporting Information (S6).

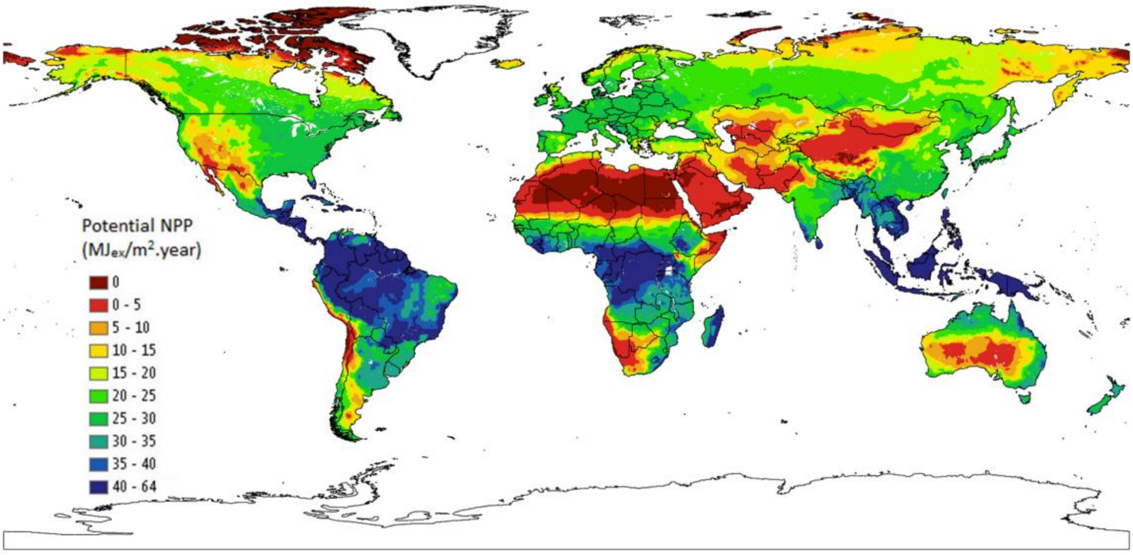

Figure 2.2: World map of characterization factors of land resources in human-made systems, based on the potential availability of natural Net Primary Production (in exergy units – MJ_{ex}/m^2.year)

Site-generic and site-dependent CF (at continent, country, region, and grid level) for human-made systems were produced through the values from this map. A site-generic CF (World average), and site-dependent CF at continent level can be seen in Table 2.1. We calculated site-dependent CF at country level for 163 countries, and site-dependent CF at regional level (administrative regions) for the six largest countries in area (Russia, Canada, China, United States, Brazil, and Australia). The full list of site-dependent CF (at country and regional level) can be seen in the Supporting Information (S7).

Table 2.1: Characterization factors for land resources (at continent level and World average), in human-made systems, with the variability of values within each area

Continent	Characterization factors (MJ_{ex}/m^2.year)	Variability of the values (MJ_{ex}/m^2.year)	
	Mean value	2.5^{th} percentile	97.5^{th} percentile
World	21.5	0.0	48.2
North America, Central America, and Caribbean	19.8	0.0	39.9
South America	35.6	4.3	51.3
Europe	23.2	11.7	29.2
Africa	19.8	0.0	48.8
Asia	18.1	0.0	47.8
Oceania and Australia	18.0	2.1	35.0

As it can be seen in Table 2.1, the average characterization factors are considerably different from each other, for instance, South America has an average CF value that is almost two times higher than North America. Besides that, except for Europe, the standard deviations are rather high. Therefore, whenever possible, it is better to use the site-dependent CF, at country, region, or grid level, which can be found in the Supporting Information (S6 and S7), for more precise values.

NPP as a quantifier for obtained products/outputs in intensive agriculture, forestry, or other human-made systems, has already been used in other LCIA methods, mainly to quantify ecosystem quality rather than for resource accounting (Baitz et al., 2000; Beck et al., 2010; Lindeijer, 2000a; Nakagawa et al., 2002; Weidema and Lindeijer, 2001). It is also used by the HANPP indicator (Erb et al., 2009; Haberl et al., 2007), that considers the potential natural NPP and agricultural yields to account for the human appropriation of NPP. Contrary to them, the method proposed in this paper, which is designed for resource accounting in LCA, uses the potential natural NPP to account for the consumption of natural land resources of human-made systems. In this sense, agricultural yields are not considered since they are technosphere outputs. In fact, our approach concentrates on how to quantify the value of land as natural resource, next to others (e.g. fossil, metals, and minerals). This is one specific aspect of land. Of course land use means also other environmental impacts next to resource use (e.g. loss of biodiversity), which need to be evaluated by other specific midpoint categories (e.g. de Baan et al. (2012)).

The uncertainties for the CF generated in this study, for human-made systems, can come basically from two sources: (1) the general exergy-biomass conversion factor and (2) the potential NPP values, obtained from Haberl et al. (2007). For the former, according to Vries (1999) the group contribution method is more precise than the β-LHV, but in some situations there was no data available to proceed calculations by the first method. The CEV of wood ("Wood, oriental beech", from Phyllis database) can have a coefficient of variation of 3% if performing calculation by the two methods mentioned above. Besides, there are already embedded uncertainties on the chemical composition of the vegetation, obtained mainly from Phyllis database. Regarding the second source, uncertainties may come from the model used (Jenkins et al., 1999; Lauenroth et al., 2006; Wang et al., 2011) and also from considerations on the input data for the model, as climate and leaf area index (Williams et al., 2001). Coefficients of variation on NPP values can range from 40% to 163%, depending on the model used (Lauenroth et al., 2006). The potential NPP values from Haberl et al. (2007) were calculated by using the Lund-Potsdam-Jena dynamic global vegetation model. Consequently, other values of potential NPP could be obtained if another model was used.

2.3.2 Practical Implementation

2.3.2.1 Case study 1

In this case study we used the site-generic $CF_{natural}$ (1.06 MJ_{ex}/MJ) for the products from natural systems. For the Brazilian Parana Pine we used the site-dependent $CF_{human\text{-}made}$ at regional level for the state of Parana (34.8 MJ_{ex}/m^2.year – Supporting Information S7); and for the Eucalyptus we used the site-dependent $CF_{human\text{-}made}$ at country level for Thailand (36.0 MJ_{ex}/m^2.year – Supporting Information S7). The CF used in the other LCIA methods can be seen in Hischier et al. (2009) and (Dewulf et al., 2007). Figure 2.3 shows the result of this case study.

By using the CF proposed in this paper, the Eucalyptus from Thailand (human-made system) had the lowest land resource consumption (13.1 GJ_{ex}/m^3), mainly due to its short growth cycle (Figure 2.3). Opposite to that, the Parana Pine from Brazil (also from human-made system) had the highest land resource consumption (212.7 GJ_{ex}/m^3). The woods from natural systems presented values in between those two (28.0 and 20.2 GJ_{ex}/m^3), and were function of the wood quality, i.e., the exergy content of the wood species (Azobe and Meranti).

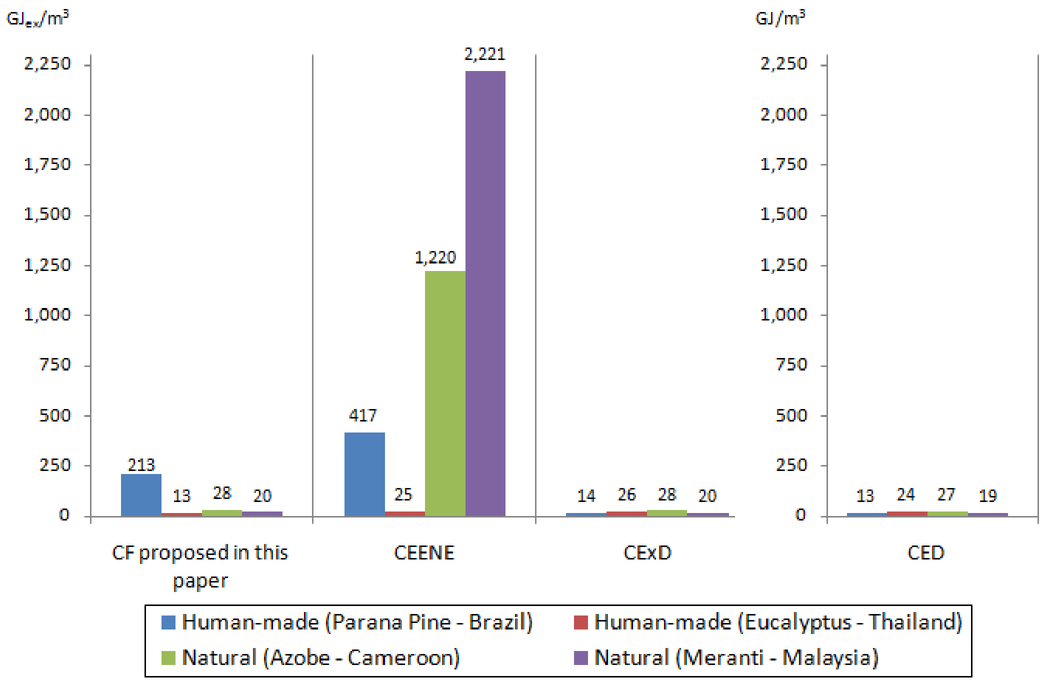

Figure 2.3: Result for case study 1 with the CF proposed in this paper, two exergy-based LCIA methods, and an energy-based LCIA method

Figure 2.3 shows that the CEENE method gave extremely high values to the natural systems, due to the extensive way the biomass is produced ($1.2{\cdot}10^3$ GJ_{ex}/m^3 and $2.2{\cdot}10^3$ GJ_{ex}/m^3). The ratio between the highest and lowest land resource consumption for 1 m^3 of wood is in the order of 90 ($2.2{\cdot}10^3$ GJ_{ex}/m^3 versus 24.5 GJ_{ex}/m^3, respectively) in this method. On the other hand, the CExD method produced more equal results, since only the exergy of the biomass is taken into account: different yields do not affect the final result. The difference between its highest and lowest values is in the order of 2 (27.8 and 13.7 GJ_{ex}/m^3, respectively). The CED method produced similar results to the CExD method, since both of them consider only the content of the wood.

Overall, a considerable diversity among the impact assessment methods was noticed, especially between the CEENE and the CExD. Although they have the same basic scientific concept (exergy), their results were unlike, due to their different choices in what to account for land resources. The CF proposed in this paper account for land resources in two different ways, combining the strengths of the CExD and the CEENE methods (biomass exergy content is taken as a starting point for the use of land resources at natural system, while the exergy related to the deprived natural potential NPP is used for accounting land resources at human-made systems). Even though the initial distinction between natural and human-made systems may sometimes not be straightforward (e.g. at natural forests), the method proposed in this paper is able to avoid double-counting of land resources, since the exergy content of the biomass and the exergy deprived from nature due to land occupation shall not be accounted together.

2.3.2.2 Case Study 2

To perform the analysis on 9 biomass products from ecoinvent (all human-made systems), first we applied the site-generic CF into the elementary flows from ecoinvent. The former database does not support completely the framework proposed in this paper, so small adaptations had to be performed while implementing the CF. A list of the elementary flows from ecoinvent, adjusted to the framework proposed in this paper, is presented in the Supporting Information (S8). Next, we considered also the site-dependent CF (at continent, country, and regional level), as presented in the Supporting Information (S7), for the direct land occupation, i.e., only for the foreground data. For all nine of them, we specified a region ourselves (7 cases) or it was specified by the ecoinvent database (products from France and Spain). Figure 2.4 shows the results of this comparison.

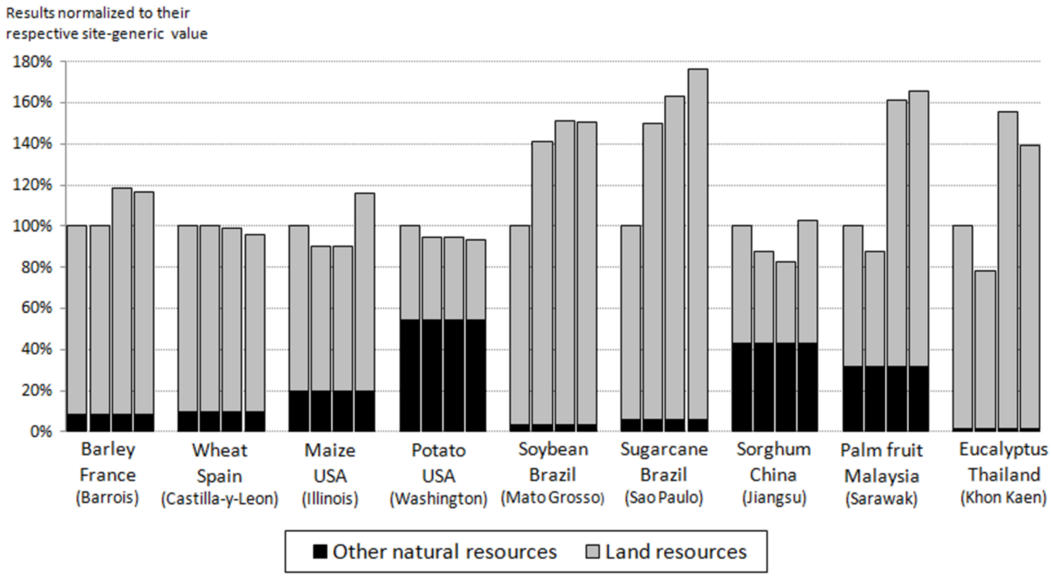

Figure 2.4: Comparison between site-generic (outer left bars), site-dependent at continent level (middle left bars), site-dependent at country level (middle right bars), and site-dependent at regional level (outer right bars) CF for 9 biomass products – showing the share of land resources in the overall resource footprint and how their spatial-differentiation can affect the final results

The land resources are represented in gray color and all the other natural resources (non-biotic renewable resources, metals, minerals, fossil fuels, nuclear energy, water resources, and atmospheric resources), are represented in black color. From Figure 2.4 we can see that the share of land resources can be very high for the products with high renewability degree (Dewulf et al., 2005), e.g. 97% for soybeans from Brazil (site-generic CF). On the other hand, potatoes from the USA, sweet sorghum from China, and palm fruit from Malaysia had a high share of other natural resources (54%, 43%, and 32%, respectively), especially water, since they are irrigated systems. These results show how land resources play an important role in the overall resource footprint of a product.

In a next step, natural resource consumption for all 9 cases were intended to be site-dependent; however, in practice only the land resources from human-made systems could be made site-dependent, relying on the CF brought forward with this paper. Except for wheat from Spain, which site-dependent CF value is similar to the site-generic CF, the variation on the final result is considerable, either giving a lower value (down to 78% for Eucalyptus in Thailand, when using site-dependent CF at continent level), or making it increase up to 177% (for sugarcane in Brazil, when using site-dependent CF at regional level). Another important aspect shown in Figure 2.4 is the direct relation between the variation of the final results due to regionalization with the renewability degree, e.g., the value of the site-dependent CF (at regional level) for Malaysia is higher than for Brazil (Supporting Information – S7), but the variation in the final results with the site-generic CF was lower (166%, while for Sugarcane in Brazil was 177%). This happened because 32% of the total exergy value from Malaysian palm fruit is from non-land resources, making the regionalization of land resources less influential in the final result than in the Brazilian sugarcane case.

From these results we could observe how the use of site-generic data can underestimate (e.g. palm fruit from Malaysia) or overestimate (e.g. potatoes from USA) the overall resource used. The CF proposed in this paper have the novelty to generate site-dependent CF at different levels (for land resources from human-made systems).

2.4 CONCLUSIONS

By clearly distinguishing between natural and human-made systems, we are able to consistently account for land resources that are actually extracted/deprived from the natural environment and/or competing with other possible human uses. Site-dependent CF for human-made systems allow spatial differentiation in the exergy calculations for LCA, which was excluded so far. A future challenge is the development of regionalized CF for other natural resources (e.g. water and metals) in exergy terms, in order to give a complete overview on regionalization of resource consumption.

CHAPTER 3: A new natural resource balance indicator for terrestrial biomass production systems[**]

ABSTRACT

Managing the efficient use of land is a key aspect, especially for a sustainable biomass-based economy. Due to the complexity in accounting all inputs for biomass production, land use efficiency analysis is usually performed without completeness, for instance, considering only fossil fuels. The objective of this paper is to introduce a new indicator, called Overall Net Annual Exergy Production (ΔEP), which considers the total biomass production from a land, the cumulative consumption of non-local resources (e.g. fossil fuels), and the natural primary biotic resource production that is deprived due to the land use, through exergy (which is the amount of useful work that can be obtained from a resource). We applied this indicator to seven agricultural case studies, composed by one or more crops, and located at different areas of the World. The case study composed by potato and wheat was the only one to generate negative ΔEP (-27.4 GJ_{ex}/ha.year), while the case studies that were composed by at least one C4 plant (maize or sugarcane) in the rotation or permanent crops (palm fruit) produced positive ΔEP. The latter had the highest ΔEP (+329.7 GJ_{ex}/ha.year). This indicator was able to give a more holistic overview of the natural resource balance of biomass production systems in comparison to the indicators commonly used in literature (e.g., *net energy value*), contrasting with the land's natural state, through a simple equation, and making use of data already available in literature.

Keywords: Land use; biomass; exergy; net primary production; provisioning service

3.1 INTRODUCTION

Due to non-renewable resource depletion and impacts related to global warming, a more biomass-based economy is arising, in which products (e.g.: fuels and chemicals) use biomass as feedstock (Bessou et al., 2011; Vandermeulen et al., 2011). At the same time, the World's population is projected to grow from 6.9 billion in 2010 to more than 9 billion in 2050

[**] Redrafted from: Alvarenga, R.A.F; Dewulf, J.; Van Langenhove, H. 2013. A new natural resource balance indicator for terrestrial biomass production systems. *Ecological Indicators*, v.32, pp 140-146.

(United Nations, 2009), promoting an increase in food demand. Regardless the final use of the biomass produced (food, fuels, or chemicals), land availability is the limiting factor. As a result, its efficient use is vital to promote a more sustainable economy.

Efficiency can be measured in the industrial sector through exergy[††] analysis, which considers the second law of thermodynamics (Dewulf et al., 2008). This analysis can be done by considering the exergy of the inputs and outputs entering and leaving the system, respectively, which is often called as 'gate-to-gate' analysis. Another way of analysis is by considering the life cycle perspective, in which the cumulative exergy consumption of the inputs are taken into account, called 'cradle-to-gate' analysis (ISO, 2006a).

Agricultural and forestry systems are not as controllable as industrial systems. In the latter it is possible to account for all the inputs and outputs, but for the former (agricultural and forestry) it is rather complex: (a) It is already difficult to account precisely for the total outputs, since crop residues and some losses due to herbivore consumption are not often considered with the productivity of the harvested portion (estimations are possible though); (b) Not all inputs can be easily accounted, especially the natural inputs, which are usually poorly considered (Zhang et al., 2010b), but some improvement in this field is available in literature, for instance the partial accounting for regulating and supporting services (Zhang et al., 2010a). Due to this complexity in managing *semi-open* systems (agriculture and forestry), usually their efficiency is measured incompletely, accounting typically only the cumulative energy consumption of the fossil fuels used in the crop production, through indicators generally named as *net energy value* (or *balance*) (Field et al., 2008; Fore et al., 2011; Franzese et al., 2009; Kamahara et al., 2010; Keoleian and Volk, 2005; Macedo et al., 2008; Papong et al., 2010). Other studies may also consider the energy/exergy from solar irradiation and from other inputs, such as fertilizers, in addition to the fossil fuels (Brehmer et al., 2008), but they still lack completeness.

The net primary production (NPP) is the biomass production from the first trophic level (autotrophic organisms), and its potential natural value, i.e., the potential NPP (NPP_{pot}), is an estimation of how much biomass production would occur in a region if not being used by humans (Haberl et al., 2007). It is reliant on several local biotic and abiotic factors, and it is the potential natural biotic production from an area. In other words, it is the biomass naturally

[††] By definition, the exergy of a resource or a system is the amount of useful work that can be obtained from it (Dewulf et al., 2008). More information can be found in Szargut et al. (1988) and Kotas (1985).

produced by using solely *in situ* solar irradiation and inputs provided by nature, i.e., local resources. According to Erb et al. (2009) and Haberl et al. (2007), the effect of land use induced change in NPP (ΔNPP_{LC}), is the difference between the actual NPP (NPP_{actual}), which is the total NPP of the crop being produced in agricultural systems, and the NPP_{pot}. These authors use the ΔNPP_{LC} as an intermediate indicator for the Human Appropriation of Net Primary Production (HANPP) index. Considering a resource balance point of view, the ΔNPP_{LC} can be positive, meaning that agricultural and forestry biomass is being produced in a higher quantity than naturally; or negative, meaning the opposite. The first situation should always be preferred, since they would be contributing to Earth's biomass availability.

A considerable difference between natural biomass production (expressed by the NPP_{pot}) and the agricultural or forestry biomass production is the consumption of non-local resources in the latter, i.e., fertilizers, irrigation, machines for sowing and harvesting, and even manpower. Therefore, even though a land might have a positive balance on ΔNPP_{LC}, the overall resource balance (including then the non-local resources) may be negative.

The objective of this paper is to introduce a new way to analyze the natural resource balance of terrestrial biomass production systems, which combines the NPP_{pot}, the NPP_{actual} (total biomass produced by humans), and the cumulative consumption of non-local resources for the man-made biomass production. This method was tested in seven land use case studies.

3.2 MATERIALS AND METHODS

3.2.1 Components of a generic biomass production system

Usually, the productivity of a biomass production system is expressed only for the main product harvested (e.g. wheat grains). Although, the grown biomass has other components that are rarely published by statistical organizations: the *above-ground residues* (e.g. leaves and stem), and the *below-ground residues* (e.g. roots). In the further analysis of this paper, we considered the whole biomass production, i.e., the main product and its above-ground and below-ground residues, in order to make a fair comparison with the NPP_{pot}, which reflects the above and below-ground primary production.

3.2.2 Exergy analysis of a biomass production system

From a 'cradle-to-gate' resource point of view, the inputs in a natural system are the solar irradiation and the other local inputs provided by nature (e.g. rainfall, wind, CO_2, etc). As output, there is a natural biomass production expressed by the NPP_{pot}. Therefore, in an exergy balance analysis, the exergy lost and destroyed (Dewulf et al., 2008) would be equal to the sum of the two inputs subtracted by the output. In a man-made system, the inputs are the solar irradiation, the local natural inputs, and the cumulative resource consumption of the non-local resources (from human inputs); and the output is the total biomass produced. Therefore, in an exergy balance analysis, the exergy lost and destroyed would be equal to the sum of the three inputs, subtracted by the output (Figure 3.1).

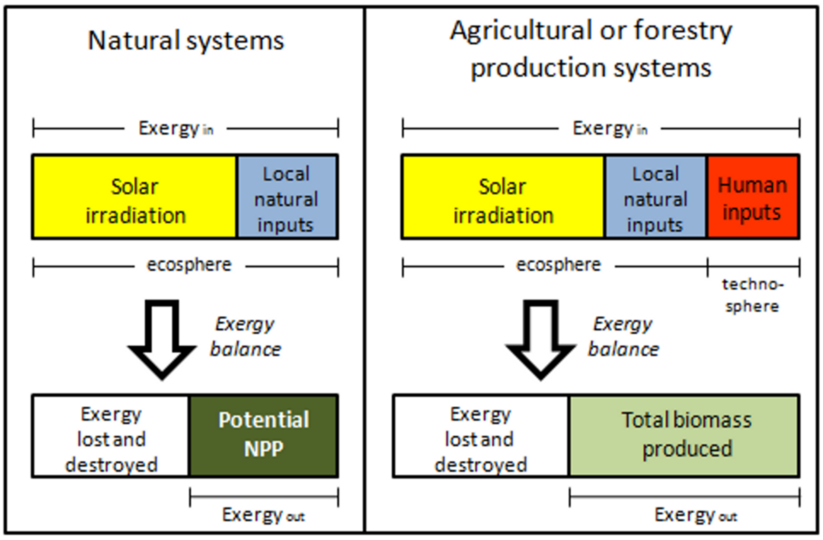

Figure 3.1: Representation of the exergy balance of biomass production of natural (left) and man-made systems (right)

It is known that when an area suffers from land use change, altering its fauna and flora, the natural inputs consumed and the fraction of solar irradiation absorbed by the flora will be different. For simplification in the further analysis, we will consider that: (1) The fraction of solar irradiation absorbed and the natural inputs consumed by the flora at a specific area, regardless its species, are the same in natural and man-made biomass production systems; and (2) the natural system is the reference and stationary state for the Earth's natural biotic production.

An exergy analysis considers the useful work that can be obtained from a system, providing the same quality for all resources (e.g.: MJ_{ex}), in spite of its renewability degree. Therefore, if the balance between the total man-made biomass produced and the cumulative consumption of non-local resources, from a specific area, is equal to the NPP_{pot} of that same specific area, the Earth's overall natural resource balance is not changed, i.e., the quality of resources made available from the Earth are kept the same, since the exergy lost and destroyed is the same. This gives the insight into a new approach for evaluating the efficiency of a particular land use, by comparing it with its natural state. A simplified representation of this new approach of evaluation can be seen in Figure 3.2.

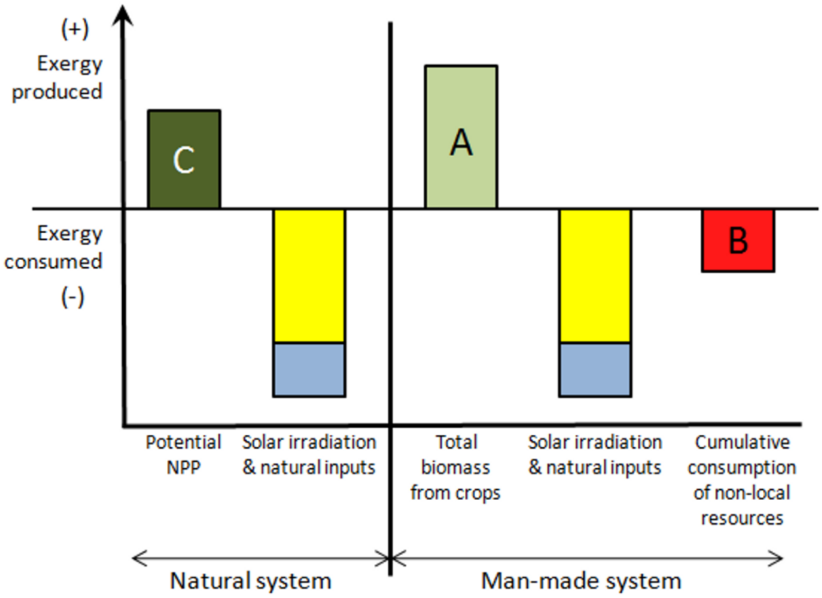

Figure 3.2: Simplified representation of the exergy balance of biomass production in natural (left) and man-made systems (right) (Bar 'A' represents the exergy produced by the total biomass from crops; bar 'B' represents the exergy consumed by the cumulative consumption of non-local resources; bar 'C' represents the exergy produced by the NPP_{pot}; yellow bars mean solar irradiation; and blue bars mean natural inputs)

3.2.3 Overall Net Annual Exergy Production (ΔEP)

The method presented in this paper makes use of exergy analysis, creating an indicator to calculate the natural resource balance of biomass production systems, the so called Overall Net Annual Exergy Production (ΔEP). It is the balance between the total annual production of biomass from the man-made system ('A' – in Figure 3.2), the annual cumulative exergy consumption (CExC) embodied in the non-local resources introduced by humans ('B' – in Figure 3.2), and the potential annual natural biomass production, or NPP_{pot} ('C' – in Figure 3.2) (Equation 3.1). The detailed mathematical calculations to get to this equation can be seen in the Supporting Information (S1).

$$\Delta EP = A - (B + C) \qquad (3.1)$$

3.2.4 Case studies

We applied the ΔEP indicator in seven man-made biomass production case studies, which were composed by one or more of the following crops: palm fruit, sugarcane, maize, soybeans, wheat, and potatoes. These crops were selected because they were the non-forage crops with highest production in the world in the last five years, together with rice, sugar beets, and cassava (not considered in the case studies) (FAO, 2012). Each case study was at a specific country and when crop rotation was applied we followed local practices. The detailed information of each case study is presented below:

Case study 1 (CS1): Production of palm fruit in Malaysia. Since this is a permanent crop, there is no crop rotation. We adopted a 25-year-cycle, in which no harvest occurs at the first three years (its establishing period), and cuts occur twice a year in the following 22 years (Brehmer, 2008). We considered this system to be irrigated, according to the ecoinvent database v2.2 (Ecoinvent, 2010).

Case study 2 (CS2): Production of sugarcane in Brazil, at the state of Sao Paulo. After planted, the first harvest of this crop is called *Plant cane*, and the following harvests are called *Ratoon*. The crop cycle can be of several years, depending on the productivity of the *Ratoon*. We adopted a crop cycle of six years with 1 cut of *Plant cane* and 4 cuts of *Ratoon* (Macedo et al., 2008). Since this is a perennial plant, no crop rotation was considered.

Case study 3 (CS3): Production of soybean and maize in Brazil, at the Center-West region. For more specific data we considered that the land was located at the state of Mato Grosso. Soybeans are usually planted between October and November, grown during summer (from southern hemisphere), and harvested during February, March, or April (Embrapa, 2010). In the same land, maize *safrinha*[‡‡] is grown during winter season. As a consequence, this case study had a time-length of one year, with soybeans and maize grown and harvested in this period.

Case study 4 (CS4): Production of maize and soybeans in the Mid-West region of the United States of America (USA). For more specific data we considered that the land was located in the state of Iowa. Maize was grown in the first year and soybean in the second year, therefore

[‡‡] Maize *Safra* is grown in the best season (summer), while *Safrinha* is grown in the winter, as crop rotation

2-year cycle with maize and soybeans grown and harvested in this period (Hernandez-Ramirez et al., 2010).

Case study 5 (CS5): Production of potatoes and wheat in the northwest of USA. For more specific data we considered that the land was located in the state of Idaho. It had a 3-year cycle, composed by the following crop rotation: potato – spring wheat – spring wheat (Myers et al., 2008). We considered the potato production system to be irrigated, according to the ecoinvent database v2.2 (Ecoinvent, 2010).

Case study 6 (CS6): Production of winter wheat, potatoes, and maize in Germany. This land use system had the following crop rotation: maize – winter wheat – potato – winter wheat (Fiener and Auerswald, 2007). It had a 4-year cycle, with winter wheat being grown and harvested twice and potato and maize once.

Case study 7 (CS7): This case study corresponded to the production of winter wheat and maize in France. This land use system had the following crop rotation: maize – winter wheat (Oorts et al., 2007). It had a 2-year cycle, with maize being grown and harvested in the first year and winter wheat planted in the first year (shortly after maize harvest) and harvested in July of the following year.

These seven case studies provide biomass for different purposes (food, feed, and/or fuel), and therefore the results of this analysis were not intended to qualify the land use systems, but purely illustrate the ΔEP indicator.

3.2.5 Source of information for the case studies

For these case studies we needed information at three levels: (a) NPP_{pot}, for natural biomass production; (b) Cumulative consumption of non-local resources; and (c) Total biomass produced (productivity, biomass components, and chemical composition of the crops).

NPP_{pot} for natural biomass production: For this source of information, we used the regionalized data on NPP_{pot} from Haberl et al. (2007), which is calculated in exergy terms for several regions in Alvarenga et al. (2013c). For CS1, CS6, and CS7 we used the country-specific values, and for CS2 and CS3 from Brazil and CS4 and CS5 from USA we used the state-specific values. The case study, country, state adopted, and NPP_{pot} (in $MJ_{ex}/m^2.yr$) can be seen in Table 3.1.

Table 3.1: Averaged natural potential net primary production (NPP_{pot}) of the area (country for CS1, CS6 and CS7 and state for CS2, CS3, CS4 and CS5) in the seven case studies. Data is based on Alvarenga et al. (2013c)

Case study	Country	State adopted	NPP_{pot} ($MJ_{ex}/m^2.yr$)[(a)]
CS1	Malaysia	-	48.30
CS2	Brazil	Sao Paulo	42.19
CS3	Brazil	Mato Grosso	38.48
CS4	USA	Iowa	29.03
CS5	USA	Idaho	15.42
CS6	Germany	-	26.50
CS7	France	-	28.04

[(a)] The unit $MJ_{ex}/m^2.yr$ stands for a certain production of exergy, expressed in MJ_{ex}, per a certain area and time, expressed in squared meters (m^2) and years (yr)

Cumulative consumption of non-local resources: To account for the cumulative consumption of non-local resources we used data from ecoinvent database v.2.2[§§] (Ecoinvent, 2010) for all crops, except maize from Brazil (CS3), which was based on Alvarenga et al. (2012). The data used from ecoinvent database were specific for the respective countries, except for maize and potato from Germany (CS6) and maize from France (CS7), which were not available in the aforementioned database and therefore we used the data from Switzerland. To transform these data into exergy terms, we calculated the cumulative resource consumption of the non-local resources through the method *Cumulative Exergy Extraction from Natural Environment (CEENE)* (Dewulf et al., 2007), and considered the values obtained in the following categories: *Renewable resources*, *Fossil fuels, Nuclear energy, Metal ores, Minerals*, *Water resources,* and *Atmospheric resources.* We did not consider the results from *Land Occupation* category to avoid double-counting with the values from the NPP_{pot}, that ought to be used for land occupation accounting in the CEENE method (Alvarenga et al., 2013c).

Total biomass produced (productivity, biomass components, and chemical composition of the crops): For all crops, we considered the chemical composition and quantities of the main product and above-ground residues according to Brehmer (2008). The exergy value of each chemical compound and the chemical composition of the biomass components of the crops can be seen in Supporting Information (S2). We assumed that the chemical exergy content (per mass of dry matter) of the below-ground residues were equal to the chemical

[§§] Ecoinvent is one of the most used databases for life cycle assessment due to its consistent and transparent datasets (www.ecoinvent.ch) exergy content of the rest of the biomass (main product and above-ground residues), due to lack of specific data on below-ground residues.

For all case studies the productivity of the main product was based on average values between 2001 and 2010. For country-specific case studies we used data from FAOSTAT (FAO, 2012) and for the case studies from Brazil and USA we used the data from national agricultural statistics agencies, for state-specific productivity (IBGE, 2011; U.S. Department of Agriculture (USDA), 2011). Moisture content of the main product and the relative amount of above-ground biomass (in dry weight) were based on Brehmer (2008). The ratio between below-ground and above-ground biomass was based on Eggleston et al. (2006), except in CS1 and CS2, which were based on Schroth et al. (2002) and Otto et al. (2009), respectively. Generally most of the data on productivity of maize is published for the grains, but the chemical composition of the main product from Brehmer (2008) refers to the maize ear. Therefore, we used an ear/grain coefficient (wet weight) of 1.18, based on Howell (2010) and Silva et al. (2010b).

Apart from this total biomass output, Haberl et al. (2007) also considered the share of what is lost during the biomass growth and the NPP of weeds, when calculating the ΔNPP_{LC}, using factors of 0.14 for industrialized countries, 0.18 for transition markets, 0.23 for developing countries, and 0.36 for least developed countries. These factors are based on estimations of crop losses due to pathogens, animal pests and weeds, from Oerke et al. (1994). Therefore, we included this factor in our case studies, but considering the same value for all of them (0.14), for simplification.

The amount of biomass harvested of each crop, the amount of above-ground residues, and the ratio between the below-ground residues and the total above-ground biomass (main product and residues), with their respective sources for the seven case studies, can be seen in Table 3.2.

Table 3.2: Averaged annual production of each biomass component for the seven case studies [a], with the respective source of information (superscript) (note that the values are annualized for one year of biomass production, which means that the sum of values within each case study represents the respective averaged biomass production of one year in one hectare, under that crop rotation system)

			Main product (kgDM[b]/ha)	Above-ground residues (kgDM[b]/ha)	Below-ground residues : above-ground biomass	Total biomass produced (kgDM[b]/ha)
CS1	Palm fruit	(1/1)	15,092 [e] [f]	14,555 [e] [f]	0.30 [c] [j]	31,223
CS2	Sugarcane	(1/1)	26,832 [f] [g]	1,980 [f] [g]	0.17 [k]	33,770
CS3	Maize (ear)	(1/1)	3,552 [f] [g] [l] [m]	4,474 [f] [g]	0.22 [i]	9,792
	Soybean	(1/1)	2,663 [f] [g]	5,403 [f] [g]	0.19 [i]	9,598
CS4	Maize (ear)	(1/2)	4,925 [f] [h] [l] [m]	6,203 [f] [h]	0.22 [i]	13,577
	Soybean	(1/2)	1,440 [f] [h]	2,922 [f] [h]	0.19 [i]	5,191
CS5	Potato	(1/3)	3,066 [f] [h]	689 [f] [h]	0.49 [d] [i]	4,093
	Wheat	(2/3)	2,750 [f] [h]	3,357 [f] [h]	0.24 [i]	7,573
CS6	Maize (ear)	(1/4)	2,102 [e] [f] [l] [m]	2,648 [e] [f]	0.22 [i]	5,795
	Wheat	(2/4)	2,972 [e] [f]	3,627 [e] [f]	0.24 [i]	8,183
	Potato	(1/4)	2,256 [e] [f]	507 [e] [f]	0.49 [d] [i]	3,011
CS7	Maize (ear)	(1/2)	4,103 [e] [f] [l] [m]	5,168 [e] [f]	0.22 [i]	11,311
	Wheat	(1/2)	2,779 [e] [f]	3,392 [e] [f]	0.24 [i]	7,651

[a] The values are normalized for one year of biomass production
[b] DM refers to the dry matter content of the biomass
[c] For Palm fruit, the ratio is between the below-ground residues and the stalk, i.e. not the fruits and leaves, where the stalk corresponds to 36% of the dry matter of above-ground residues
[d] For potatoes, the ratio is between below-ground residues (i.e., non-tuber) and the above-ground residues
[e] Based on FAO (2012)
[f] Based on Brehmer (2008)
[g] Based on IBGE (2011)
[h] Based on U.S. Department of Agriculture (USDA) (2011)
[i] Based on Eggleston et al. (2006)
[j] Based on Schroth et al. (2002)
[k] Based on Otto et al. (2009)
[l] Based on Howell (2010)
[m] Based on Silva et al. (2010b)

3.3 RESULTS AND DISCUSSION

3.3.1 Case studies

After calculating the ΔEP for the seven case studies, we normalized all the results for one year of biomass production. The results of biomass production, specified by each component of each crop, the cumulative consumption of non-local resources (by CEENE method), and the NPP_{pot} of each case study are presented in Table 3.3.

We applied the indicator ΔEP to the values from Table 3.3, obtaining the results shown in Table 3.4. For a broader interpretation of the results, we also included the indicator ΔNPP_{LC}, from Erb et al. (2009) and Haberl et al. (2007), and the Net Energy Value (NEV) (Field et al., 2008; Fore et al., 2011; Franzese et al., 2009; Kamahara et al., 2010; Keoleian and Volk, 2005; Macedo et al., 2008; Papong et al., 2010). These results can also be visualized by Figure 3.3.

Table 3.3: The biomass produced (separated by each component), the cumulative consumption of non-local resources (separated by fossil fuels, water, and other resources), and the natural potential net primary production (NPP_{pot}) for each case study (values are in GJ_{ex}/ha.yr)

Case studies	CS1	CS2	CS3	CS4	CS5	CS6	CS7
Country	Malaysia	Brazil	Brazil	USA	USA	Germany	France
Crops	Palm fruit	Sugarcane	Maize, Soybeans	Maize, Soybeans	Potatoes, wheat	Maize, wheat, potatoes	Maize, wheat
Total biomass produced	960.6	698.7	437.7	419.4	248.6	369.3	441.5
Main product	522.7	494.3	131.5	129.6	110.7	141.1	134.7
Above-ground residues	291.3	38.2	194.0	180.8	78.5	133.3	169.3
Below-ground residues	32.6	91.6	66.6	65.6	32.9	56.5	69.3
Weeds and lost biomass	114.0	74.6	45.6	43.5	26.5	38.4	68.2
Total non-local resources consumed	147.9	13.2	27.1	22.3	121.8	31.3	31.1
Cumulative fossil fuels consumption	25.5	10.8	22.2	18.0	30.5	26.2	27.0
Cumulative water resources consumption	107.1	0.9	1.5	1.9	85.4	1.1	1.1
Cumulative consumption of other resources [(a)]	15.3	1.5	3.3	2.4	5.9	4.0	3.0
NPP_{pot}	483.0	421.9	384.8	290.3	154.2	265.0	280.4

[(a)] 'Other resources' is a sum of the following CEENE categories: *Renewable resources*, *Metals ores*, *Minerals*, and *Nuclear energy*

Table 3.4: Results of the seven case studies in overall net annual exergy production (ΔEP), introduced in this paper, in land use induced change in NPP (ΔNPP_{LC}) from Erb et al. (2009) and Haberl et al. (2007), and in net energy value (NEV), widely used in literature (values are in GJ_{ex}/ha.yr)

Case studies	CS1	CS2	CS3	CS4	CS5	CS6	CS7
Country	Malaysia	Brazil	Brazil	USA	USA	Germany	France
Crops	Palm fruit	Sugarcane	Maize, Soybeans	Maize, Soybeans	Potatoes, wheat	Maize, wheat, potatoes	Maize, wheat
ΔEP	329.7	263.6	25.8	106.9	-27.4	73.0	130.0
ΔNPP_{LC}	477.6	276.8	52.9	129.2	94.4	104.3	161.2
NEV	497.2	483.6	109.3	111.6	80.2	114.9	107.7

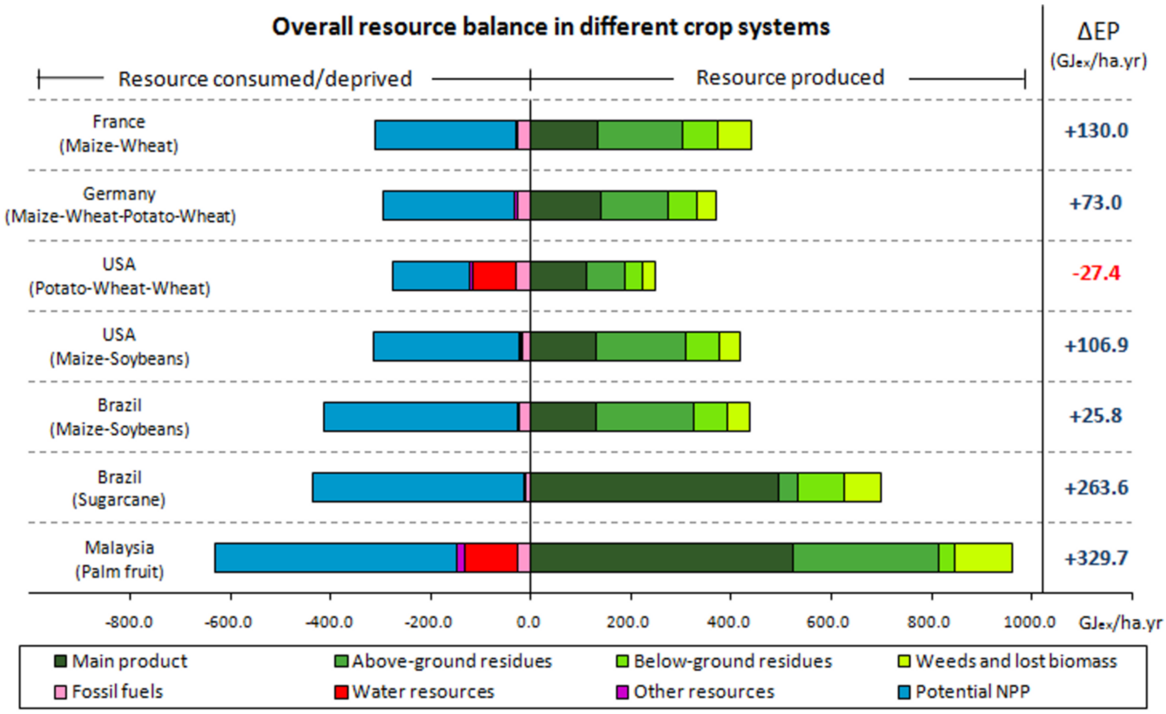

Figure 3.3: Illustration of the overall resource balance (expressed in exergy per area and time – $GJ_{ex}/m^2.yr$) and the overall net annual exergy production (ΔEP) for the seven case studies. Resources produced (right) are detailed by biomass compartment (e.g. above-ground residues) and resources consumed/deprived (left) are detailed by the potential net primary production and the type of resource consumed (e.g. fossil fuels) ('Other resources' is the sum of the following CEENE categories: renewable resources, metals ores, minerals, and nuclear energy)

CS1 (palm fruit – Malaysia) had the highest ΔEP (+329.7 GJ_{ex}/ha.yr), which was influenced by the high total biomass production (960.6 GJ_{ex}/ha.yr), that was able to overcome the high NPP_{pot} (483.0 GJ_{ex}/ha.yr) and the high consumption of water resources (107.1 GJ_{ex}/ha.yr), among other resources. CS2 (sugarcane – Brazil) had the second highest ΔEP (+263.6 GJ_{ex}/ha.yr), mainly due to the high total biomass production (698.7 GJ_{ex}/ha.yr) and the lowest consumption of non-local resources (13.2 GJ_{ex}/ha.yr). CS3 (maize-soybean – Brazil) had a low, but still positive, ΔEP (+25.8 GJ_{ex}/ha.yr), which was mainly influenced by the high NPP_{pot} (384.8 GJ_{ex}/ha.yr) associated to a low productivity of maize (Table 3.2). CS4 (maize-soybean – USA) was composed by the same crops of CS3, but they were grown over 2 years, double of the time from the previous case study. Due to the high productivity of maize (Table 3.2) and a moderate NPP_{pot} (290.3 GJ_{ex}/ha.yr), the ΔEP was rather elevated (+106.9 GJ_{ex}/ha.yr). CS5 (potato-wheat – USA) was the only case study with negative ΔEP (-27.4 GJ_{ex}/ha.yr), meaning that humans hinder and extract overall more resources from the environment than what is being produced. The NPP_{pot} from this case study is rather low (154.2 GJ_{ex}/ha.yr), which is a result (among other factors) of the dry climate from that region.

Nevertheless, the ΔEP generated was negative due to the high consumption of water resources (85.4 GJ_{ex}/ha.yr) and fossil fuels (30.5 GJ_{ex}/ha.yr), associated with the absence of C4 plants, which generally have higher productivities. Finally, CS6 (maize-wheat-potato – Germany) and CS7 (maize-wheat – France) produced positive ΔEP (73.0 and 130.0 GJ_{ex}/ha.yr, respectively), which were mainly characterized by median NPP_{pot} values (265.0 and 280.4 GJ_{ex}/ha.yr, respectively), high total biomass productivity (369.3 and 441.5 GJ_{ex}/ha.yr, respectively), and low consumption of water resources.

The ΔEP indicator is sensitive to all components involved in equation 3.1, but a special attention should be given to the productivity of the main product. This data directly influences the estimation of the total biomass produced (since the productivity of the above-ground and below-ground residues are reliant on that), and it is influenced by the cumulative consumption of non-local resources. The source of information for all the data used in the indicator ΔEP was mentioned in the Material and Methods section, and a discussion on its quality is out of the scope of this paper.

3.3.2 Discussion of the ΔEP indicator

The difference between the indicator proposed in this paper (ΔEP), and the ΔNPP_{LC}, brought in by Erb et al. (2009) and Haberl et al. (2007), is the introduction of the cumulative consumption of non-local resources. The results from ΔNPP_{LC} in Table 3.4 were always positive and higher than the ΔEP, which can give misleading interpretations, e.g., we could have concluded that CS5 (potato-wheat – USA) produced more resources than natural production by considering solely the ΔNPP_{LC} (+94.4 GJ_{ex}/ha.yr), but the cumulative consumption of the non-local resources that are brought to this system are very high (121.8 GJ_{ex}/ha.yr), and actually the overall natural resource balance is negative, as shown by the ΔEP indicator. Apart from the ΔNPP_{LC}, several other studies make use of another class of indicators, generally called as *net energy value* (or *balance*) (Field et al., 2008; Fore et al., 2011; Franzese et al., 2009; Kamahara et al., 2010; Keoleian and Volk, 2005; Macedo et al., 2008; Papong et al., 2010), which considers the other two of the three components from ΔEP: the harvested main product and the cumulative consumption of fossil fuels. This type of indicator considers only the *technosphere* aspect, i.e., the variables involved are the inputs from humans and outputs to humans. This is interesting for industrial systems, but when a semi-open system is evaluated, it may be incomplete and overestimate the energy balance. This can be corroborated by our results from Table 3.4, such as CS3 (maize-soybean – Brazil) and CS4 (maize-soybean – USA), which have approximately the same value for NEV (+109.3 and +111.6 GJ_{ex}/ha.yr), but when we also consider the natural biomass production, by the ΔEP indicator, their results become very different (+25.8 and +106.9 GJ_{ex}/ha.yr). Besides, since it considers only the consumption of fossil fuels, other resources are simply neglected, giving again rise to misleading interpretations. This is the case in CS5 (potato-wheat – USA), where the NEV was positive (+80.2 GJ_{ex}/ha.yr), not only because it did not account for the NPP_{pot}, but also because it neglected the consumption of water resources for irrigation. These results corroborates that ΔEP is able to give a more complete representation for natural resource balance of biomass production systems, in comparison to the ΔNPP_{LC} and NEV indicators.

The methodology from Zhang et al. (2010a) appears to have a satisfactory completeness in direct and indirect consumption of natural inputs, but it is still complex and a comparison with the land's natural state is not made available, as with the ΔEP. The ΔEP indicator is also applicable to non-biomass production land use systems, as ground-mounted solar panels. In this case, the only difference would be to consider the exergy produced by the solar panels, instead of the exergy produced by the biomass, while the cumulative consumption of non-local resources and the NPP_{pot} would still be used in the equation.

The case studies presented in this paper were mainly illustrative, representing the results that could be obtained by using the ΔEP indicator and its advantages over traditional indicators. The ΔEP can also be applied to more specific case studies, for instance at a specific farm, based on the data provided by the user. Moreover, the ΔEP can be applied to dynamic systems, such as the *Orchidee-FM* model for forestry (Bellassen et al., 2011a; Bellassen et al., 2011b), where forest NPP was modeled in function of different management practices. By the ΔEP, an optimal resource balance could be achieved, reliant on the (cumulative) inputs needed for the management practices (e.g. fossil fuels consumed for tree thinning) and the NPP outputs, with and without the management practices.

3.4 CONCLUSIONS

The ΔEP indicator is an improvement of the well known *net energy value* and the ΔNPP_{LC}, since it considers the total biomass produced, the NPP_{pot} (ignored in the *net energy value*, but considered in the ΔNPP_{LC}), and the cumulative consumption of non-local resources (ignored in the ΔNPP_{LC}, but partially considered in the *net energy value*). Even though the approach may be criticized by not considering changes in the natural inputs and solar irradiation consumption due to land use change, the ΔEP is able to provide a natural resource balance of the actual land use, in comparison to its natural state, through a simple equation from which the variables are already available in literature.

The ΔEP ought to be used to give a complete overview on the balance of Earth's natural resources, evaluating the efficiency of land use in order to promote a more environmentally sustainable biomass-based economy. In this sense, it is important to mention that the indicator presented here is dedicated to a resource production point of view, i.e. provisioning services. While certain man-made systems seem to be more efficient than natural systems, this does not mean that they generate only benefits, since other ecosystem services (regulating, supporting, and cultural services) may be affected when a natural land is transformed for biomass production for humans.

CHAPTER 4: Life cycle assessment of bioethanol-based PVC. Part 1: Attributional approach***

ABSTRACT

Literature suggests that depletion of non-renewable resources is the most concerning environmental impact category in the life cycle of the polyvinyl chloride (PVC), mainly due to the fossil feedstock for ethylene. Therefore, bioethanol is considered as another source for ethylene in the PVC production chain. The objective of this paper was to perform a cradle-to-gate attributional life cycle assessment of bioethanol-based PVC resin. We created two scenarios for bioethanol-based PVC (2010 and 2018), and compared them with fossil-based PVC. We used primary data from Solvay S.A. and secondary data from literature, for the life cycle inventory. For the impact assessment, we used several midpoint indicators and the Recipe Endpoint H/A. At midpoint level, bioethanol-based PVC from 2010 and 2018 presented better results than fossil-based PVC for non-renewable resource use (13.8, 13.4, and 44.8 MJ_{ex}/kg of PVC resin, respectively) and climate change (-0.09, -0.19, and 1.52 kg CO_2eq/kg of PVC resin, respectively), but worse results for other environmental impact categories (e.g. ecotoxicity). At endpoint level, the two bioethanol-based PVC scenarios showed better results overall than fossil-based PVC (up to 66% lower). Within the bioethanol-based PVC scenarios, the results for 2018 were better than for 2010 (up to 43% lower for the endpoint single score results) corroborating that higher efficiency (at the crop field and bioethanol production) and reduction of burnt harvest ought to reduce environmental impacts. Even though bioethanol-based PVC had better results in comparison to fossil-based, improvements should be sought to minimize other environmental impact categories, e.g., biodiversity and ecotoxicity.

Keywords: PVC, bioethanol, LCA, bio-based, environmental impact.

4.1 INTRODUCTION

Polyvinyl chloride (PVC) is a thermoplastic that has been produced in industrial scale since the first half of the 20th century and, thanks to its versatility, found applications in many

*** Redrafted from: Alvarenga, R.A.F; Dewulf, J.; De Meester, S.; Wathelet, A.; Villers, J.; Thommeret, R.; Hruska, Z. 2013. Life cycle assessment of bioethanol-based PVC. Part 1: Attributional approach. *Biofuels, Bioproducts and Biorefining*, DOI: 10.1002/bbb.1405 economic sectors (e.g. construction and packaging). The global demand for PVC exceeded 30 million metric tonnes in 2009 and it is in constant growth (+5% on global average), especially in developing countries (http://www.pvc.org/en/). Ethylene and chlorine are the two main feedstocks needed to manufacture PVC. While the supply of chlorine is virtually inexhaustible, the availability of fossil-based ethylene is limited to the end of the *petrochemical era*. When using Life Cycle Assessment (LCA) to evaluate the environmental impacts in the life cycle of PVC, the depletion of fossil fuels was considered to be the most concerning environmental impact category (Salazar and Sowlati, 2008; Stripple et al., 2008), and the production stages until the vinyl chloride monomer (VCM) were the main contributors (Baitz et al., 2004; Baitz et al., 2005). These conclusions can be corroborated by assessing PVC from ecoinvent database (Ecoinvent, 2010), through several life cycle impact assessment (LCIA) methods, as presented in the Supplementary Material (SM-1).

In this sense, and in addition to society's pressure on environmental impacts related to global warming and resource depletion, new technologies are being developed to manufacture ethylene from renewable raw materials, such as converting bioethanol into (bio)ethylene by dehydration (Martinz and Quadros, 2008; Morschbacker, 2009). Bioethanol may come from different biomass sources, but sugarcane is the main raw material for this commodity in Brazil, one of the biggest producers in the world (Cerqueira Leite et al., 2009; Goldemberg and Guardabassi, 2010). Its production is projected to grow even more in the future, induced by increasing internal and external demands (UNICA (www.unica.com.br) and CTBE (http://www.bioetanol.org.br/)). Bioethanol has been used as source of fuel in Brazil for more than 30 years and its efficiency and environmental impacts have been extensively discussed in literature (Brehmer and Sanders, 2009; Cavalett et al., 2013; Cavalett et al., 2011; Macedo et al., 2008; Ometto et al., 2009; Seabra et al., 2011). Due to legislation and governmental-industry agreements (Governo do Estado de Sao Paulo, 2002; UNICA, 2007), the harvest of sugarcane involving burning techniques will be gradually reduced in the upcoming years, decreasing the environmental impacts as well (De Figueiredo and La Scala Jr, 2011; Garbiate et al., 2011; Gullett et al., 2006; Maioli et al., 2009; Silva et al., 2010a).

Several sources of biomass have been considered as alternative materials in the chemical industry for the so-called *bio-based plastics* (Alvarez-Chavez et al., 2012; Chen and Patel, 2011; Groot and Borén, 2010; Hermann et al., 2010; Khoo and Tan, 2010; Khoo et al., 2010; Lammens et al., 2011; Liptow and Tillman, 2012; Urban and Bakshi, 2009), but no consistent environmental assessment of bioethanol-based PVC has been found in literature. There are basically two modeling approaches in LCA: attributional and consequential (Finnveden et al., 2009). The first describes the environmentally relevant physical flows related to the life cycle of the product, while the latter describes how environmentally relevant flows can change in response to the life cycle of the same product. The objective of the first part of this work was to perform a cradle-to-gate LCA of bioethanol-based PVC considering the attributional approach, and using the fossil-based PVC as benchmark. The consequential approach was assessed in the second part of this work (Alvarenga et al., 2013b).

4.2 MATERIAL AND METHODS

4.2.1 Goal and scope

We performed a cradle-to-gate LCA of bioethanol-based and fossil-based PVC. The functional unit considered was 1 kg of PVC resin, at the factory gate. The system boundaries are visualized in Figure 4.1.

The replacement of fossil-based by bio-based feedstock is still in its initial phases in the chemical industry, and comparing these two feedstocks may give misleading interpretations since the fossil-based feedstock has an established and mature technology while the bio-based feedstock still has room for improvement. For this reason, we considered two scenarios for bioethanol-based PVC, based on Macedo et al. (2008): (1) referring to bioethanol production from 2010, with 62% of the sugarcane harvested through burning techniques; (2) referring to a prognosis of bioethanol for the future (year 2018), with technological advances and efficiency improvements at the sugarcane field and bioethanol mill, and with 16% of the sugarcane harvested through burning techniques (see details in Supplementary Material (SM-2)).

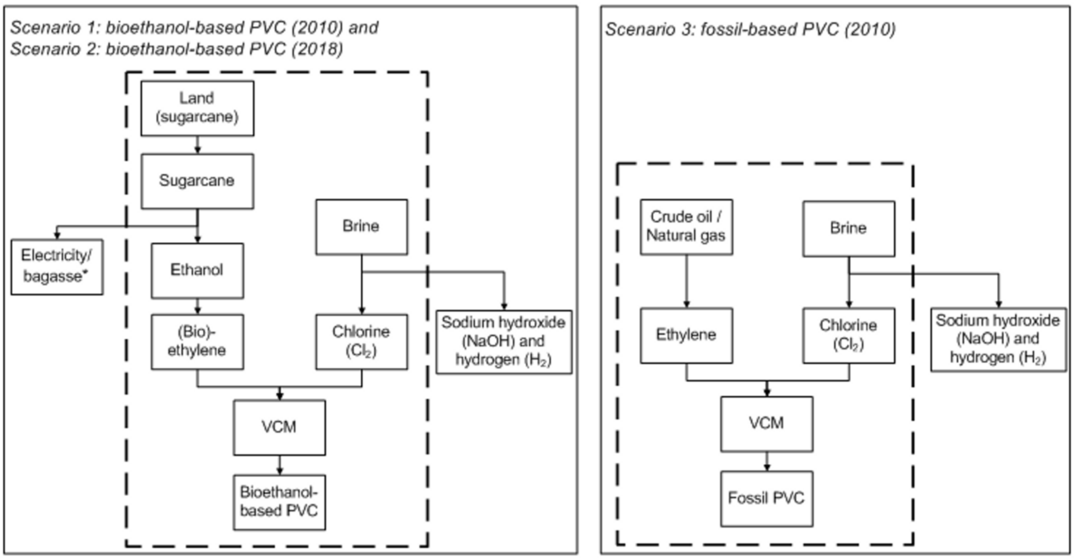

Figure 4.1: Simplified flowchart of bioethanol-based PVC (left) and fossil-based PVC (right), expressing the system boundaries with the dotted lines for the main raw materials used (*bagasse was a co-product in 2010, while in 2018 it was entirely used for energy and electricity production)

4.2.2 Life Cycle Inventory (LCI)

For bioethanol-based PVC, the LCI of the sugarcane and bioethanol production was based on several sources from literature, and can be visualized in the Supplementary Material (SM-2). In the fossil-based PVC, data for the ethylene production was based on ecoinvent database (Ecoinvent, 2010). The LCI of the other foreground production phases, whether referring to bioethanol-based or fossil-based PVC, were based on primary data from Solvay Indupa do Brasil S.A. The electricity use in all stages of the foreground data was based on the Brazilian electricity mix (available at ecoinvent database), except for the bioethanol production process, which does not require electricity from the grid, since energy is produced from the bagasse. The data for the background processes were based on ecoinvent database. A summary of the source of data for the LCI can be found in Table 4.1.

Table 4.1: Summary of the source of data for the life cycle inventory

Production stage	PVC scenario	Source of data for the LCI	Origin of the data:
Sugarcane production	Bioethanol-based PVC (2010), Bioethanol-based PVC (2018)	Several secondary data (see details in SM–2)	Brazil
Bioethanol production	Bioethanol-based PVC (2010), Bioethanol-based PVC (2018)	Several secondary data (see details in SM–2)	Brazil
(bio)ethylene	Bioethanol-based PVC (2010), Bioethanol-based PVC (2018)	Solvay Indupa do Brasil S.A.	Brazil
Ethylene (fossil)	Fossil-based PVC (2010)	ecoinvent database v2.2	Europe
Chlorine production	Bioethanol-based PVC (2010), Bioethanol-based PVC (2018), Fossil-based PVC (2010)	Solvay Indupa do Brasil S.A.	Brazil
VCM production	Bioethanol-based PVC (2010), Bioethanol-based PVC (2018), Fossil-based PVC (2010)	Solvay Indupa do Brasil S.A.	Brazil
PVC resin production	Bioethanol-based PVC (2010), Bioethanol-based PVC (2018), Fossil-based PVC (2010)	Solvay Indupa do Brasil S.A.	Brazil
Other background data	Bioethanol-based PVC (2010), Bioethanol-based PVC (2018), Fossil-based PVC (2010)	ecoinvent database v2.2	Brazil and Europe (mainly)

4.2.3 Life Cycle Impact Assessment (LCIA)

For LCIA, midpoint and/or endpoint (Bare et al., 2000) indicators can be used to assess the environmental impacts of products. Midpoint indicators represent points in the cause-effect chain of a particular impact category (e.g. acidification potential), prior to the endpoint indicators, which represent the end of the cause-effect chain (e.g. damage to the Natural Environment) (Bare et al., 2000). Several debates on these two approaches already occurred in the LCA community and a discussion between their advantages and disadvantages is out of scope of this paper. In our LCA, we used both midpoint and endpoint indicators.

To be consistent between the midpoint and endpoint analysis, we considered the same environmental impact categories (Table 4.2), which are separated in three areas of protection: Resources, Ecosystems, and Human Health. For resources at midpoint level we considered the CEENE method (Dewulf et al., 2007), updated with the methodology from Alvarenga et al. (2013c) for land resources, dividing them in three categories: (1) *Renewable resources* (biomass from natural systems, land occupation, wind energy, and hydropower energy); (2) *Water resources*; and (3) *Non-renewable resources* (fossil fuels, nuclear energy, minerals, and metals). For *biodiversity* impacts due to land use, we used spatial-differentiated characterization factors from de Baan et al. (2012). *Human toxicity* and *ecotoxicity* were assessed through the USEtox method (Rosenbaum et al., 2008). For climate change we used the method IPCC 2007 (100a) (IPCC, 2007). Since most of the PVC products have a long life-time (e.g., water pipes and windows for housing), we considered the PVC resin from this paper as carbon sink. Therefore, we accounted for the uptake of CO_2 in bioethanol-based PVC, and the biogenic CO_2 emissions until the PVC factory gate, in the climate change category. For the other environmental impact categories, i.e., *eutrophication*, *acidification*, *photochemical oxidant formation*, *particulate matter formation*, *ozone depletion*, and *ionizing radiation*, we used the method Recipe midpoint (version 1.06) (Goedkoop et al., 2010).

Because the results of the midpoint analysis may not be a straightforward guidance for decision making, we also performed an analysis at endpoint level with the method Recipe Endpoint (version 1.06) (Goedkoop et al., 2010), a LCIA methodology created by several institutes from The Netherlands. Although this method lacks on resources and spatial differentiation for land use impacts, we chose to use it because it goes beyond the mandatory elements set by ISO 14040 (ISO, 2006a), providing also data on weighting and normalization factors. For normalization we used the World factors provided by the method, and for weighting factors we used the Hierarchist version, therefore *World Recipe Endpoint H/A*, where 'H' stand for Hierarchist and 'A' stand for average weighting set. Results were analyzed at the areas of protection *Resources*, *Ecosystems*, and *Human Health*, and also through single score, represented as ecopoints (Pt), which is obtained after normalization and weighting of the endpoint categories. For the climate change impacts, we considered characterization factors for biological CO_2 uptake and emissions.

Table 4.2: Methods used for the life cycle impact assessment phase, at midpoint and endpoint levels

Environmental impact category	Area of protection	Method used at Midpoint	Method used at Endpoint
Renewable resources	Resource	CEENE (Alvarenga et al., 2013c; Dewulf et al., 2007)	-
Water resources	Resource	CEENE (Dewulf et al., 2007)	-
Non-renewable resources	Resource	CEENE (Dewulf et al., 2007)	Recipe Endpoint (Goedkoop et al., 2010)
Biodiversity (land use)	Ecosystems	de Baan et al. (2012)	Recipe Endpoint (Goedkoop et al., 2010)
Ecotoxicity	Ecosystems	USEtox (Rosenbaum et al., 2008)	Recipe Endpoint (Goedkoop et al., 2010)
Acidification	Ecosystems	Recipe Midpoint (Goedkoop et al., 2010)	Recipe Endpoint (Goedkoop et al., 2010)
Eutrophication	Ecosystems	Recipe Midpoint (Goedkoop et al., 2010)	Recipe Endpoint (Goedkoop et al., 2010)
Climate change	Ecosystem and Human Health	IPCC 2007 (100a) (IPCC, 2007)	Recipe Endpoint (Goedkoop et al., 2010)
Human toxicity	Human Health	USEtox (Rosenbaum et al., 2008)	Recipe Endpoint (Goedkoop et al., 2010)
Photochemical oxidant formation	Human Health	Recipe Midpoint (Goedkoop et al., 2010)	Recipe Endpoint (Goedkoop et al., 2010)
Particulate matter formation	Human Health	Recipe Midpoint (Goedkoop et al., 2010)	Recipe Endpoint (Goedkoop et al., 2010)
Ozone depletion	Human Health	Recipe Midpoint (Goedkoop et al., 2010)	Recipe Endpoint (Goedkoop et al., 2010)
Ionising radiation	Human Health	Recipe Midpoint (Goedkoop et al., 2010)	Recipe Endpoint (Goedkoop et al., 2010)

4.2.4 Allocation

Within our foreground data, two process units generated co-products and allocation was needed: (a) In the chlorine production we performed a mass-based allocation among its co-products (NaOH and H_2), the commonly used allocation method in this industrial sector; (b) In bioethanol production we performed an exergetic allocation among the co-products (bagasse and electricity at scenario 1 and just electricity at scenario 2). In this system we needed to make an allocation correction for the carbon uptake, to ensure that the net carbon uptake was present solely in the bioethanol, and not allocated between the co-products.

4.2.5 Uncertainty analysis

For uncertainty analysis, we used the simplified approach with a pedigree matrix (Frischknecht et al., 2007) to estimate the standard deviation of the inputs and outputs within each process unit of our study. Afterwards, we performed a Monte Carlo analysis, by the software Simparo 7.3 (with 100 runs and a confidence interval of 95%), analyzing the uncertainty of the LCI data.

4.3 RESULTS AND DISCUSSION

4.3.1 Midpoint (several LCIA methods)

The results of the midpoint indicators are presented in Table 4.3 and in Figure 4.2, where the LCI uncertainty values were plotted together. The results of the category *Ionising radiation* presented very high uncertainties (97.5 percentile values were up to 5.5 times higher than the mean value), and are not totally visible at Figure 4.2. We can see that the use of non-renewable resources and the climate change impacts were lower in bioethanol-based than in fossil-based PVC scenarios. For all other impact categories, the fossil-based PVC presented better results. These results can be corroborated by the studies from Khoo et al. (2010), Groot and Borén (2010), Urban and Bakshi (2009), and Weiss et al. (2012), where other bio-based chemicals are compared to their fossil-based equivalent products.

Table 4.3: Result of the attributional LCA for 1 kg of PVC resin (for the three scenarios), from cradle-to-gate, at midpoint level

Environmental impact categories	Unit	Bioethanol-based PVC (2010)	Bioethanol-based PVC (2018)	Fossil-based PVC (2010)
Renewable resources	MJ_{ex}	8.55E+01	7.10E+01	5.76E+00
Water resources	MJ_{ex}	4.45E+00	3.43E+00	1.37E+00
Non-renewable resources	MJ_{ex}	1.38E+01	1.34E+01	4.48E+01
Biodiversity (land use)	BDP	1.03E+00	8.48E-01	1.89E-02
Ecotoxicity	CTUe	3.74E+00	3.05E+00	6.47E-03
Acidification (terrestrial)	kg SO_2 eq	1.87E-02	1.32E-02	3.08E-03
Eutrophication (fresh water)	kg P eq	4.17E-04	3.23E-04	5.25E-06
Eutrophication (marine)	kg N eq	1.09E-03	8.19E-04	3.04E-04
Climate change	$kgCO_2eq$	-9.31E-02	-1.89E-01	1.52E+00
Human toxicity	CTUh	4.96E-10	4.48E-10	3.80E-10
Photochemical oxidant formation	kg NMVOC	1.48E-02	7.69E-03	4.04E-03
Particulate matter formation	kg PM_{10} eq	1.27E-02	5.43E-03	1.10E-03
Ozone depletion	kg CFC-11 eq	7.37E-08	7.10E-08	4.45E-08
Ionising radiation	kg U235 eq	2.66E-02	2.51E-02	1.68E-02

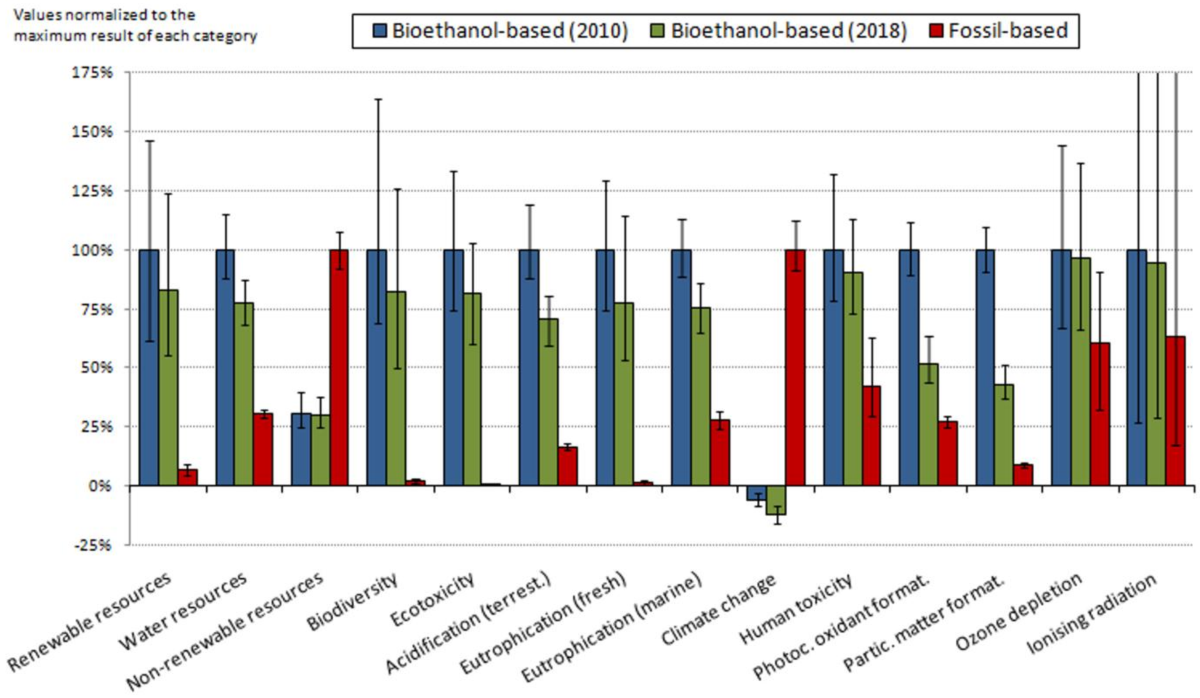

Figure 4.2: Results of the attributional LCA for 1 kg of PVC resin (for the three scenarios), from cradle-to-gate, at midpoint level with LCI uncertainties, normalized to their maximum value of each category

Regarding the use of renewable resources in the bioethanol-based PVC scenarios, more than 90% responded to the occupation of agricultural land for sugarcane cultivation and approximately 8% responded to the use of electricity from the Brazilian electric mix. At the fossil-based PVC, 98% of the renewable resource use was due to Brazilian electricity consumption. With reference to the use of water resources, approximately 80% occurred at the bioethanol production process, in the bioethanol-based PVC scenarios; while in the fossil-based PVC 55% of the water was used at the fossil ethylene production process and its supply chain. Concerning the non-renewable resources, the consumption of fossil fuels were the responsible for most of the results. For bioethanol-based PVC scenarios, approximately 75% were from natural gas and diesel (consumed in several processes); while for fossil-based PVC, 80% was due to ethylene production (fossil feedstock). Regarding renewability degree analysis, based on the results from Table 4.3, we can see that from the overall resources used, 13%, 15%, and 86% were non-renewable resources in the bioethanol-based PVC (2010), bioethanol-based PVC (2018), and fossil-based PVC, respectively.

In the climate change category, greenhouse gas emissions and CO_2 uptake can be divided in 4 groups: (a) Uptake of CO_2; (b) Biogenic emissions (CO_2, CO, or CH_4); (c) CO_2 emissions due to direct land use change; and (d) Fossil emissions (CO_2, CO, CH_4, N_2O, SF_6, among others). In case of bioethanol-based PVC scenarios, CO_2 was absorbed (a) by the sugarcane and the leaves (trash). From that, a share was reemitted to the environment in the form of biogenic emissions (b), mainly in the trash burning (during sugarcane harvest), the fermentation of bioethanol, or the energy production in the bioethanol factory, and corresponded to approximately 85% of the total emissions. There was also emission of CO_2 due to the direct land use change (c), that corresponded to approximately 2% of the total emissions in the bioethanol-based scenarios (from this value, approximately 30% was from the sugarcane production and 70% was from the Brazilian electricity mix, i.e., hydropower energy). The fossil emissions (d) responded to approximately 13% of the total emissions in the bioethanol-based scenarios (from this value, 33% and 28% were up to the agricultural gate, mainly soil emissions and diesel burning, for 2010 and 2018 respectively). In the fossil-based PVC, biogenic emissions (b) and emissions from direct land use change (c) were responsible for 5% and 7% of the total emissions (both emissions were due to use of electricity), respectively. The remaining 88% were related to fossil emissions (d), from which approximately 55% was from the ethylene production process. A negligible amount of CO_2 was absorbed, by electricity consumption (which was reemitted by biogenic emissions). See details in Supplementary Material (SM-3).

The impacts on biodiversity were linear to the land use values from the LCI, i.e., they were much higher in bioethanol-based PVC scenarios due to land use in the agricultural phase (sugarcane production). In the fossil-based PVC, negligible values were accounted, mainly due to hydroelectricity use and oil extraction. The human toxicity values were mainly due to use of Brazilian electricity and the VCM production process in all three scenarios, with additional impacts in the bioethanol-based scenarios due to emission of pesticides at the production of sugarcane. At the ecotoxicity category, the values in the bioethanol-based PVC scenarios were mainly due to the emission of pesticides used in the production of sugarcane. For the acidification category, most of the emissions from bioethanol-based PVC (2010) were due to soil emissions and trash burning; while in bioethanol-based PVC (2018) it was mainly due to soil emissions, since less trash was burned. In the fossil-based PVC case, more than half of the emissions came from the ethylene production process. Freshwater eutrophication was caused mainly due to phosphorus emissions in the sugarcane production, while marine eutrophication was mainly due to soil emissions from fertilizer use (e.g., NH_3 and NO_x), but also from emissions at the PVC production. The burning of trash was responsible for 65% of the photochemical oxidant formation and 74% of the particulate matter formation in bioethanol-based PVC (2010). In all scenarios, the impacts on ozone depletion were mostly related to the production of oil and the transportation of natural gas. The ionizing radiation impacts were all related to consumption of nuclear energy.

Within the bioethanol-based scenarios, bioethanol-based PVC (2018) presented better results than bioethanol-based PVC (2010) in all environmental impact categories. The main reason was the higher efficiency considered in bioethanol-based (2018), i.e., higher productivity in the sugarcane field, higher bioethanol yield, and higher production of electricity (co-product of bioethanol), which led to different allocation values. Additionally, the lower share of burnt trash during sugarcane harvest (considered to be 16% in 2018, while 62% in 2010) significantly contributed to lower environmental impact potential on several categories, especially eutrophication (marine), acidification (terrestrial), photochemical oxidant formation, and particulate matter formation.

We could see that there is a shift of environmental impacts between the bioethanol-based and fossil-based PVC scenarios, but we cannot know to what extent the lower impacts on climate change and use of non-renewable resources in the bioethanol-based PVC cases can compensate the higher impacts of the other environmental impact categories, by simply using these midpoint indicators. Therefore an additional analysis at endpoint level appears to be necessary, and is presented in the next section.

4.3.2 Endpoint (Recipe Endpoint H/A)

As mentioned before, we cannot know to what extent the shift of environmental impacts between bioethanol-based and fossil-based scenarios at midpoint level contributed or not to lower the environmental footprint at the different areas of protection. Therefore, in order to give more concrete conclusions, we assessed the environmental impacts at endpoint level as well, and these results at the characterization stage can be seen in Table 4.4.

Table 4.4: Result of the attributional LCA for 1 kg of PVC resin (for the three scenarios), from cradle-to-gate, at damage stage of Recipe Endpoint method

Environmental damage categories	Unit	Bioethanol-based PVC (2010)	Bioethanol-based PVC (2018)	Fossil-based PVC (2010)
Resources	Dollars ($)	5.02E+00	4.89E+00	1.66E+01
Ecosystems	Species.year	1.15E-09	6.86E-10	1.26E-08
Human Health	DALY	3.04E-06	1.13E-06	2.41E-06

Due to lower use of fossil fuels, bioethanol-based PVC scenarios had approximately 30% of the value from the fossil-based PVC for the *Resources* endpoint category (Table 4.4). Additionally, due to good results on climate change, the value at the endpoint category *Human Health* of bioethanol-based PVC (2018) was also lower than in the fossil-based PVC, while bioethanol-based PVC (2010) had the highest value for this category. At the *Ecosystem* endpoint category in the bioethanol-based PVC scenarios, the good results of climate change made this category to have low values, even though they caused high impacts on biodiversity, ecotoxicity, and eutrophication.

Following the methodology of the Recipe Endpoint H/A method, i.e., normalizing the results from Table 4.4 with World values and weighting them according to the Hierarchist version, we obtained single score values, that are presented in Figure 4.3, in which the uncertainties of the LCI were plotted as well. We can see that, overall, bioethanol-based PVC scenarios had better results than the fossil-based PVC: The fossil-based PVC had the highest potential environmental impact (0.23 ecopoints), followed by bioethanol-based PVC (2010) (0.14 ecopoints), and finally, with the best overall results, bioethanol-based PVC (2018) (0.08 ecopoints).

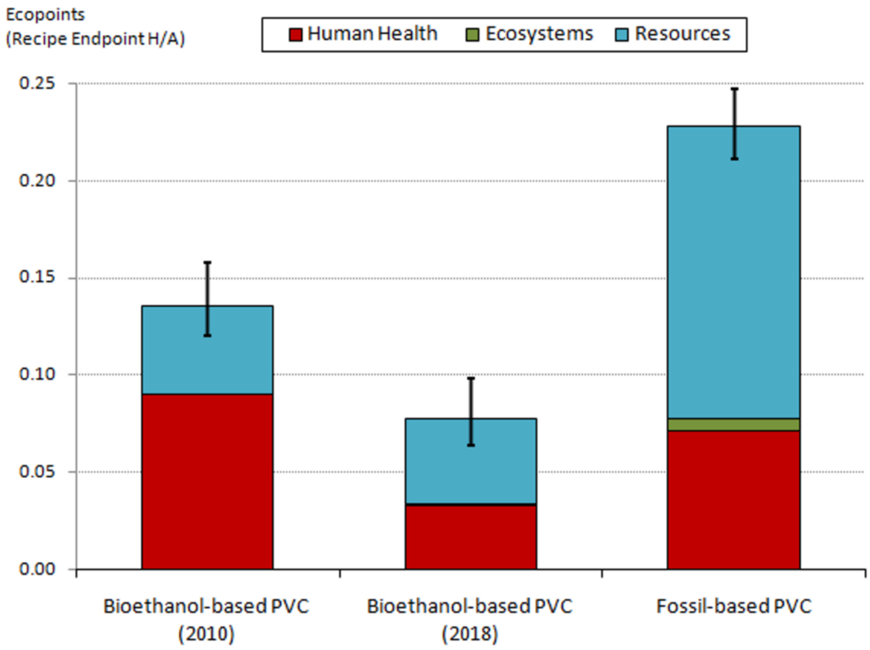

Figure 4.3: Results of the attributional LCA for 1 kg of PVC resin (for the three scenarios), from cradle-to-gate, at single score stage of the Recipe Endpoint H/A method, with LCI uncertainties

4.4 CONCLUSIONS

Bioethanol-based PVC scenarios presented lower environmental impacts than fossil-based PVC for use of non-renewable resources and climate change impacts. Even though the gains at the midpoint level appeared to be only in the aforementioned environmental impact categories, bioethanol-based PVC appeared to be better than fossil-based PVC overall, when using a single score endpoint LCIA method. It was possible to see an environmental improvement for bioethanol-based PVC (2018), up to 43% for the endpoint single score results, in comparison to bioethanol-based PVC (2010).

The shift of materials from fossil to bio-based sources is a trend in the chemical industry. Bioethanol-based PVC already showed good results in comparison to fossil-based PVC with respect to climate change and use of non-renewable resources, but improvements should be sought to minimize the environmental impacts at other categories. Inside the chemical industry boundaries, a possible improvement is to increase the bioethanol-to-ethylene efficiency, which currently is approximately 10% lower than the theoretical value (1.70 kg ethylene/kg bioethanol). Considering the bioethanol supply chain, higher sugarcane productivity at the field, higher bioethanol yield at the mill, and a lower fraction of trash burning in the sugarcane harvest already showed better results. There is still room for improvement, though, for instance we considered that by the year 2018 the amount of trash burnt during the sugarcane harvest would reduce from 62% (in 2010) to 16%, but it can be even 0%, as long as all sugarcane producers from the state of Sao Paulo follow the governmental-industry agreement (UNICA, 2007).

CHAPTER 5: Life cycle assessment of bioethanol-based PVC. Part 2: Consequential approach[†††]

ABSTRACT

From the results of the attributional life cycle assessment (LCA) of the bioethanol-based polyvinyl chloride (PVC), shown in the first part of this work, changing the feedstock from fossil to bioethanol-based ethylene appears to be a way for decreasing the environmental impacts of that product on climate change and non-renewable resources. Although, other environmental concerns may rise related to the effects of indirect land use change (iLUC) caused by sugarcane expansion. Therefore, the objective of the second part of this work was to make a consequential LCA of the bioethanol-based PVC, assessing the effects of iLUC as the key side-effect of the implementation of that product in the market on 2018, at different degrees of iLUC (three scenarios were created). The life cycle inventory was collected from literature, databases, and primary data from Solvay S.A. We used midpoint and endpoint indicators for life cycle impact assessment. At the midpoint indicators, the environmental impact categories responded differently for the different degrees of iLUC, and some of them generated gains to the environment in the three scenarios, including non-renewable resource use. At endpoint level, the results showed overall environmental gains if iLUC was kept below 5.7% of the sugarcane cultivation area. The effects of iLUC are based on assumptions, and therefore subject to uncertainties, but the assessment performed in this paper was important to provide quantitative information for the stakeholders on how the environmental gains of the bioethanol-based PVC should not be nullified by iLUC impacts.

Keywords: PVC, bioethanol, LCA, bio-based, environmental impact, iLUC.

5.1 INTRODUCTION

In order to decrease its environmental footprint, the chemical industry is seeking for renewable feedstocks, and for polyvinyl chloride (PVC) products, ethylene produced from bioethanol appears to be a good replacement for the fossil ethylene (Martinz and Quadros, 2008; Morschbacker, 2009). In the first part of this work the environmental impacts of the

[†††] Redrafted from: Alvarenga, R.A.F; Dewulf, J.; De Meester, S.; Wathelet, A.; Villers, J.; Thommeret, R.; Hruska, Z. 2013. Life cycle assessment of bioethanol-based PVC. Part 2: Consequential approach. *Biofuels, Bioproducts and Biorefining*, DOI: 10.1002/bbb.1398

Brazilian bioethanol-based PVC were assessed through an attributional life cycle assessment (LCA), using the fossil-based PVC as benchmark, showing better results for use of non-renewable resources, climate change, and for the weighted single score endpoint results (Alvarenga et al., 2013a). However, by an attributional LCA we could not evaluate environmental aspects that might emerge if bioethanol-based PVC induces an extra demand for bioethanol.

Bioethanol, the feedstock for that product, has been used as fuel for vehicles in Brazil for more than 30 years. An increased demand of bioethanol is expected in the near future, not only due to the internal demand from the expansion of the flex-fuel vehicle industry (UNICA (www.unica.com.br)), but also due to an upcoming bio-based economy (Kircher, 2012; Stevens, 2008). Improvements on the sugarcane productivity and bioethanol yield are seen as ways to support this extra demand, but they may not be enough, leading to expansion of sugarcane cultivation fields as well (Goldemberg and Guardabassi, 2010). The harvested area of sugarcane in Brazil, which is approximately 3% of the country's agricultural area, increased from 51,000 km^2 in 2002 to more than 85,000 km^2 in 2009 (FAO, 2012). This expansion, at the center-south region of Brazil, occurred mainly on pasture lands (Adami et al., 2012; Rudorff et al., 2010; Sparovek et al., 2009) and this trend is expected not to change in the future (Manzatto et al., 2009; Nassar et al., 2008). For the same period (2002 - 2009), forested areas in Brazil decreased approximately 3% (from 5.40E+06 km^2 to 5.22E+06 km^2) (FAO, 2012). Since pasture lands appear to be one of the causes of deforestation in the Brazilian Amazon forest, some studies correlated them with those that were once displaced for sugarcane cultivation (Lapola et al., 2010). This type of analysis is done by evaluating the effects of indirect land use change (iLUC) (Fritsche, 2011; Fritsche et al., 2010).

However, evaluating iLUC impacts caused by a specific product may not be straightforward, involving many uncertainties (Adami et al., 2012). In fact, it may never be possible to physically observe iLUC (Eurpean Commission, 2010), neither to blame the responsibility of land conversion of a particular area due to the introduction of biofuel and bioliquid policy, therefore modeling appears to be necessary in order to evaluate the impacts of iLUC (Eurpean Commission, 2010). Most models are based on scenario analysis, which usually draws a *baseline* scenario (with limited biofuel use) and a *policy* scenario (with promotion of biofuels), and then the impacts of iLUC are calculated through the differences between these two scenarios, divided by the difference in biofuel production within the scenarios (Eurpean Commission, 2010).

The effects of iLUC may be incorporated in LCA of products through a consequential approach (Guinée et al., 2011; Sanchez et al., 2012). Therefore, the objective of the second part of this work is to make a consequential LCA of the bioethanol-based PVC, analyzing the iLUC induced by the aforementioned product as the key side-effect; effects of market development (e.g. rebound effect and market mechanisms) were not considered in this study.

5.2 MATERIAL AND METHODS

5.2.1 Goal and scope

In the consequential approach, we analyzed only the bioethanol-based PVC (2018) from the first part of this work, and considered the fossil-based PVC as avoided product. The functional unit used was the same as in the first paper, i.e., 1 kg of bioethanol-based PVC resin at the gate. The differences between bioethanol-based and fossil-based PVC were up to the ethylene production, therefore the system boundaries for consequential approach could be shortened to that stage (Figure 5.1) (Earles and Halog, 2011; Ekvall and Weidema, 2004; Zamagni, 2012). Allocation has to be avoided through system expansion in the consequential approach (Earles and Halog, 2011; Zamagni, 2012); therefore, for the electricity generated in the bioethanol production, we considered the marginal electricity (Finnveden et al., 2009; Zamagni, 2012) for the year 2018 from the Brazilian grid as avoided product.

Since the bioethanol-based PVC (2018) might have significant environmental consequences due to indirect land use changes, we used the principle of consequential LCA to analyze these environmental impacts (Sanchez et al., 2012). There is no consensus in the scientific community on models to calculate these effects, though. In addition, most sources of literature regarding iLUC present information solely at a final stage, i.e. providing only the GHG emissions from iLUC, while just a few provide also data at intermediate level, i.e., the amount of area suffering from iLUC due to a certain amount of ethanol (from sugarcane) produced. Lapola et al. (2010) considered that the area of iLUC due to sugarcane cultivation would be equal to an equivalence of 1:1, using a scenario analysis modeling and a partial equilibrium model of the economy of the agricultural sector. This means that for every hectare of new sugarcane cultivation, one hectare of Brazilian natural vegetation would be indirectly cleared. According to the same authors, this equivalence could be 0:1, i.e., no iLUC, if pasture density would change from 0.70 to 0.83 head/ha (Lapola et al., 2010). Also based on scenario analysis, the Brazilian Land Use Model (BLUM) (Nassar et al., 2011), a one-country multiregional partial equilibrium economic model, resulted in a total land area of 267,384,000 ha in Brazil for agricultural and pasture production in 2022 for the baseline scenario, while for the policy scenario the land area needed was 267,628,000 ha. In the policy scenario there was an extra production of 9,408,000 ton of bioethanol, which we considered to be fully responsible for the additional 244,000 ha (267,628,000 – 267,384,000 ha) of land needed. Through personal communication with the authors of the report (Nassar et al., 2011), we obtained the information that the bioethanol yield considered was 6.3 m^3/ha. So, to produce the extra amount of 9,408,000 ton bioethanol in the policy scenario, 1,763,403 ha was needed. Dividing the area of natural vegetation suffering LUC (244,000 ha) by the additional area needed for bioethanol (1,763,403 ha), we could obtain an iLUC equivalence of 0.13:1.

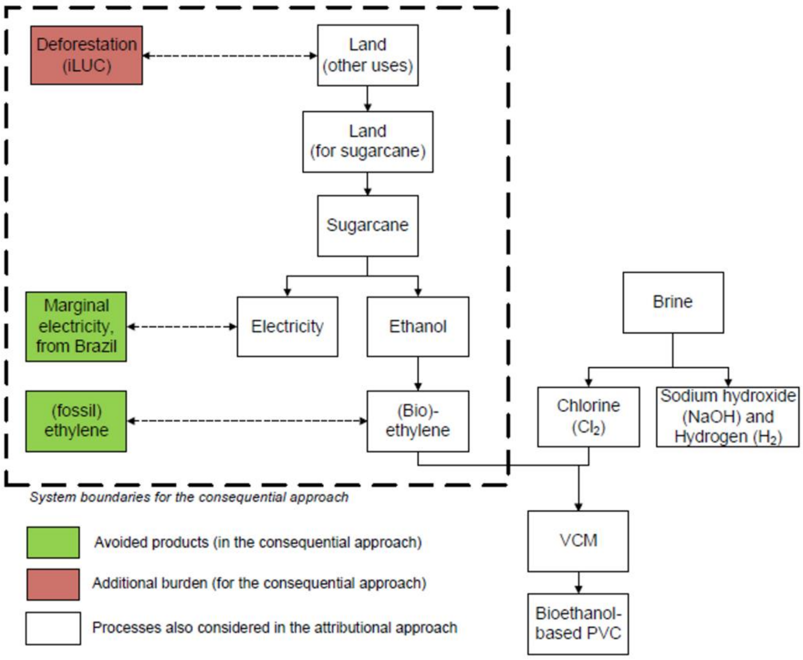

Figure 5.1: System boundaries of the consequential approach

Therefore, in the consequential approach we considered three scenarios, expressed in Table 5.1. In the consequential LCA of the bioethanol-based PVC we considered the marginal production of bioethanol, i.e., we assessed only the bioethanol coming exclusively from new areas of sugarcane cultivation. In other words, we did not consider the average bioethanol produced in Brazil in the year 2018, from which a share would be from new areas, that caused iLUC, and another share would be from established sugarcane areas.

Table 5.1: Scenarios for the consequential approach

	Scenario A	Scenario B	Scenario C
iLUC equivalence	1:1	0.13:1	0:1
Based on:	Lapola et al. (2010)	BLUM (Nassar et al., 2011)	Lapola et al. (2010)

5.2.2 LCI

The life cycle inventory (LCI) of bioethanol (and the co-production of electricity) was based on several sources from literature and is the same one available in the first part of this work (Alvarenga et al., 2013a), except for data related to land use change (LUC), which is discussed in the next paragraph. For the (bio)ethylene production we based on primary data from Solvay S.A, and for the fossil-based ethylene we used secondary data from the ecoinvent database (Ecoinvent, 2010). For the marginal electricity avoided from the Brazilian electric grid, we used the variation between the values of electricity mix of 2010 and 2018 (Table 5.2), based on the ten-year plan (2010 – 2020) for the expansion of electricity supply of the Brazilian Ministry of Mines and Energy (MME, 2011).

Table 5.2: Marginal Brazilian electricity for the year 2018, considered for the consequential approach, based on the Brazilian Ministry of Mines and Energy (MME, 2011)

Source	2010 (MW)	2018 (MW)	Marginal value (MW)
Hydropower	86,745	115,149	28,404
Nuclear	2,007	3,412	1,405
Natural gas	9,180	11,659	2,479
Coal	1,765	3,205	1,440
Fuel oil	2,371	8,790	6,419
Diesel oil	1,497	1,121	-376
Industrial gas	686	686	0
Biomass	4,496	8,333	3,837
Wind	831	9,532	8,701
TOTAL	109,578	161,887	52,309

While in the attributional LCA only the direct LUC (dLUC) was accounted and based on measured data from the past (between 2003 and 2009) (Rudorff et al., 2010), in the consequential approach we based the LUC on assumptions for the future, supported by literature. First, for dLUC, we considered that the entire area of sugarcane cultivation was previously pasture land, since this is a trend for the future (Manzatto et al., 2009; Nassar et al., 2008) (and since we analyzed only the bioethanol from new sugarcane lands). Moreover, we considered that these pasture lands, displaced by sugarcane cultivation, would move into areas with natural vegetation, which in this study was assumed to be the Amazon Forest, causing a

LUC from Amazon Forest to pasture lands (considered to be the iLUC of the bioethanol-based PVC). To translate the LUC impacts to our functional unit (1 kg of PVC resin), it is necessary to distribute them into a certain period, which commonly is 20 or 30 years (Eurpean Commission, 2010; Khatiwada et al., 2012). We could not find in literature specific period values for iLUC and, since the Renewable Energy Directive from the European Union (Eurpean Union, 2009) suggests to use 20 years for the emissions of greenhouse gases due to dLUC, we divided the impacts from the direct and indirect LUC by that value. Therefore, the annualized (Khatiwada et al., 2012) area of land transformed from pasture to sugarcane cultivation (dLUC) and from natural forest to pasture (iLUC) were 0.094 m^2, since we needed 1.88 m^2a of land occupation for 1 kg of bioethanol-based PVC resin (our functional unit), and we divided it by 20 years. For CO_2 emission due to land transformation, which is based on changes of the content of soil organic carbon (SOC), we used the methodology from European Commission (European Commission, 2010). For the forest clearing (from iLUC), we used the process 'Provision, stubbed land, BR', from ecoinvent database (Jungbluth et al., 2007), a site-specific dataset for the Brazilian Amazon forest with completeness quality provided. In this particular dataset it is considered that 20% of the aboveground biomass would be burned during the deforestation process. The elementary flows for the iLUC can be seen in Table 5.3.

Table 5.3: Elementary flows of the iLUC process considered for the consequential approach, for 1kg of bioethanol-based PVC resin produced (For scenario A we considered the full values, while for scenarios B and C 13% and 0% of these values were considered, respectively)

Elementary flow	Value	Unit
Transformation, from natural forest	0.094	m^2
Transformation, to pasture	0.094	m^2
'Provision, stubbed land/BR'	0.094	m^2
CO_2, land transformation	0.049	kg

5.2.3 Life cycle impact assessment (LCIA) and uncertainty analysis

In the consequential approach we considered the same life cycle impact assessment (LCIA) methods used in the attributional LCA (Table 5.4) (Alvarenga et al., 2013a), both for the midpoint and endpoint levels. It is important to highlight that while at midpoint level the analysis was performed at each environmental impact category (e.g. eutrophication), at endpoint level the analysis was performed through endpoint damage categories, i.e., Resources, Ecosystems (composed by the aggregation of impacts from ecotoxicity, acidification, eutrophication, biodiversity loss due to land use, and climate change), and

Human Health (composed by the aggregation of impacts from climate change, human toxicity, photochemical oxidant formation, particulate matter formation, ozone depletion, and ionizing radiation), based on the methodology from the Recipe Endpoint H/A (Goedkoop et al., 2010); and also through single score results. This is possible through normalization and weighting factors provided by the Recipe Endpoint H/A (Goedkoop et al., 2010).

Table 5.4: Methods used for the life cycle impact assessment phase, at midpoint and endpoint levels

Environmental impact category	Area of protection	Method used at Midpoint	Method used at Endpoint
Renewable resources	Resource	CEENE (Alvarenga et al., 2013c; Dewulf et al., 2007)	-
Water resources		CEENE (Dewulf et al., 2007)	-
Non-renewable resources		CEENE (Dewulf et al., 2007)	Recipe Endpoint (Goedkoop et al., 2010)
Biodiversity (land use)	Ecosystems	de Baan et al. (2012)	Recipe Endpoint (Goedkoop et al., 2010)
Ecotoxicity		USEtox (Rosenbaum et al., 2008)	Recipe Endpoint (Goedkoop et al., 2010)
Acidification		Recipe Midpoint (Goedkoop et al., 2010)	Recipe Endpoint (Goedkoop et al., 2010)
Eutrophication		Recipe Midpoint (Goedkoop et al., 2010)	Recipe Endpoint (Goedkoop et al., 2010)
Climate change	Ecosystem and Human Health	IPCC 2007 (100a) (IPCC, 2007)	Recipe Endpoint (Goedkoop et al., 2010)
Human toxicity	Human Health	USEtox (Rosenbaum et al., 2008)	Recipe Endpoint (Goedkoop et al., 2010)
Photochemical oxidant formation		Recipe Midpoint (Goedkoop et al., 2010)	Recipe Endpoint (Goedkoop et al., 2010)
Particulate matter formation		Recipe Midpoint (Goedkoop et al., 2010)	Recipe Endpoint (Goedkoop et al., 2010)
Ozone depletion		Recipe Midpoint (Goedkoop et al., 2010)	Recipe Endpoint (Goedkoop et al., 2010)
Ionising radiation		Recipe Midpoint (Goedkoop et al., 2010)	Recipe Endpoint (Goedkoop et al., 2010)

The procedure to calculate the environmental impacts of bioethanol-based PVC through the consequential approach can be visualized in Figure 5.2. First, to obtain an environmental load for the (bio)ethylene, we performed a system expansion for the electricity co-produced (at the bioethanol production) with the marginal supply. Then, from the environmental load of the (bio)ethylene we subtracted the value of the fossil ethylene, since the former shall replace the latter (fossil ethylene is an avoided product). Finally, we added the environmental impacts of the iLUC of the bioethanol, according to each scenario (A, B, or C).

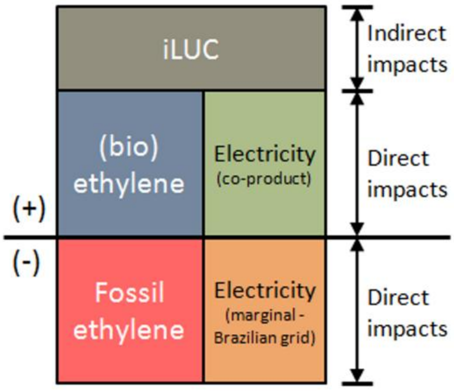

Figure 5.2: Representation of the methodology to assess the bioethanol-based PVC resin through consequential LCA

For uncertainty analysis we applied the same methodology as in the attributional approach (Alvarenga et al., 2013a). So we used the pedigree matrix (Frischknecht et al., 2007) to generate standard deviations on the inputs and outputs within each unit process of our study, followed by a Monte Carlo analysis through the software Simapro 7.3 (with 100 runs and a confidence interval of 95%).

5.3 RESULTS AND DISCUSSION

5.3.1 Midpoint (several LCIA methods)

The results of the LCA at midpoint level are shown in Figure 5.3, with the uncertainties of LCI plotted together. The uncertainties of the categories *ozone depletion* and *ionizing radiation* were high (2.5 percentile down to 5.5 times lower than the mean value) and are not completely visualized in Figure 5.3.

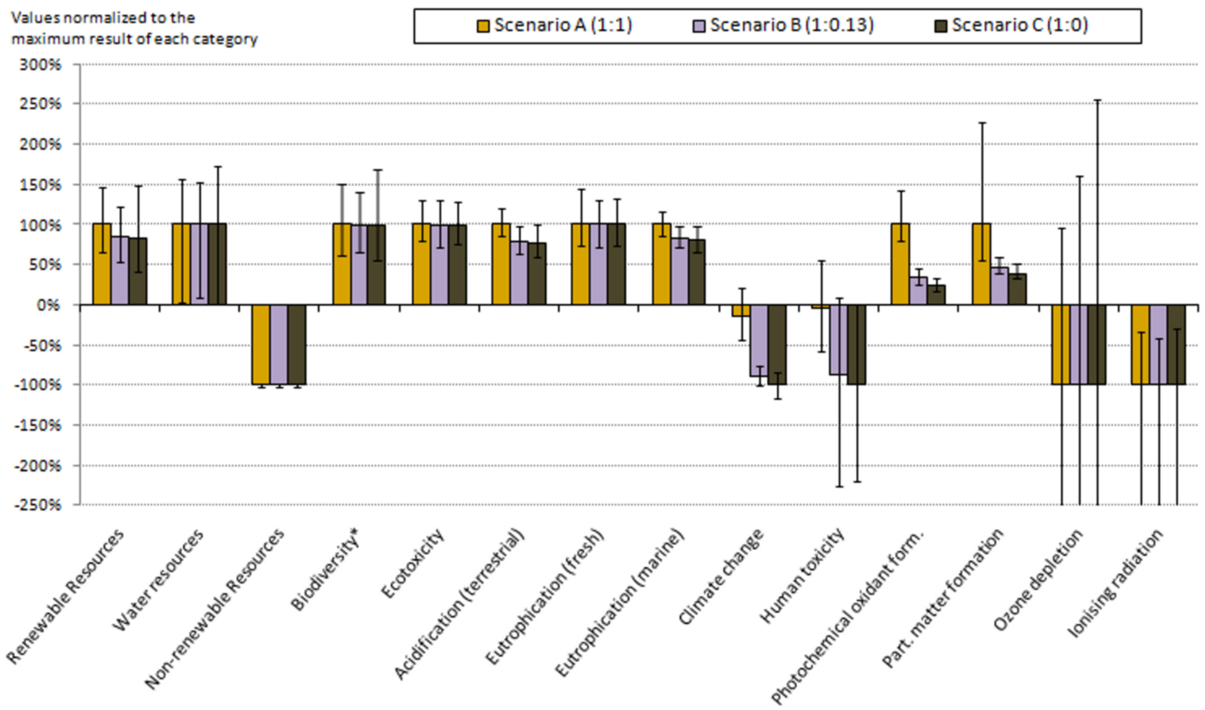

Figure 5.3: Results of the consequential LCA for 1 kg of PVC resin (for the three scenarios), at midpoint level with LCI uncertainties, normalized to their maximum value of each category (*the category *Biodiversity* was not affected by the different degrees of iLUC due to limitation of the method used)

As we can see, some environmental impact categories were not affected by the degree of iLUC (variations among scenarios were up to 2%). The categories *non-renewable resources* and *ionizing radiation* presented always negative results, meaning that the shift from fossil ethylene to (bio)ethylene would always bring environmental gains in these categories, independent of how much iLUC may occur, since the latter does not contribute to impacts in these environmental impact categories. On average, the category *ozone depletion* also presented negative results in all three scenarios, but the uncertainties on LCI generated results that were not significantly different from zero. On the other hand, the categories *water resources*, *biodiversity*, *ecotoxicity*, and *eutrophication (fresh)*, presented always positive results, meaning that the shift from fossil ethylene to (bio)ethylene would always cause higher environmental impacts on these categories (based on the mean values), independent of how much iLUC may occur, since iLUC did not contribute to the degree of the environmental impact in these categories. The category *biodiversity* was not affected by the degree of iLUC because, even though the method from de Baan et al. (2012) is spatially differentiated, it does not provide characterization factors for land use change due to high uncertainties on regeneration time.

The categories *renewable resources*, *acidification (terrestrial)*, and *eutrophication (marine)* had moderate variations in function of iLUC, i.e., the values of scenario A were up to 32%

higher than the values of scenario C. These results mean that the shift from fossil ethylene to (bio)ethylene will always enhance environmental impact in these categories, and that the degree of iLUC determines its extent. The categories *photochemical oxidant formation* and *particulate matter formation* were deeply affected by iLUC, giving values in scenario A up to four times higher than in scenario C, mainly due to impacts of biomass burning during the deforestation process (the process from ecoinvent database assumes that 20% of the biomass is burnt during deforestation) (Jungbluth et al., 2007). These results mean that the shift from fossil ethylene to (bio)ethylene will always affect these categories, and that the degree of iLUC significantly determines the magnitude of the impact.

On average, the impacts on *climate change* and *human toxicity* looks to be reduced by changing from fossil to bioethanol-based ethylene. However, for scenario A in *climate change*, and scenario A, B, and C in *human toxicity*, the reduction is limited and looks not to be significantly different from zero (considering the uncertainties in the LCI). The absolute values from the *climate change* category can be seen in Table 5.5 for the three scenarios. We can see that the amount of carbon uptake, biogenic emissions, emissions due to dLUC, and fossil emissions were constant among the scenarios, since they were not affected by the degree of iLUC. Regarding the emissions due to iLUC, approximately 96% of it was due to the burning of above-ground biomass during the deforestation process, and only 4% due to changes in the SOC content. The main reason for this was the low difference of SOC between natural vegetation and pasture lands, from which the data was based on the European Commission report (European Commission, 2010). Considering that 1kg of bioethanol-based PVC needs approximately 1 kg of bioethanol (Alvarenga et al., 2013c), the combined values of dLUC and iLUC from our study (Table 5.5) are comparable to the study from Khatiwada et al. (2012), which had (direct and indirect) LUC emissions between 0.14 and 1.23 kg CO_2 eq / kg bioethanol.

Table 5.5: Absolute values for climate change, at midpoint level, for the three scenarios from the consequential life cycle assessment of 1 kg of bioethanol-based PVC

	Scenario A ($kg\ CO_2eq$)	Scenario B ($kg\ CO_2eq$)	Scenario C ($kg\ CO_2eq$)
Uptake of CO_2 [a]	-9.11	-9.11	-9.11
Biogenic emissions	7.39	7.39	7.39
Fossil emissions [b]	-0.55	-0.55	-0.55
dLUC	0.70	0.70	0.70
iLUC	1.34	0.17	0.00
Total net emissions	-0.23	-1.40	-1.57

[a] the values in uptake are negative because they are not treated as emissions
[b] the values in fossil emissions are negative because they are avoided

5.3.2 Endpoint (Recipe Endpoint H/A)

The results of the endpoint analysis can be seen in Table 5.6. The category *resources* showed negative results for all three scenarios, showing that the shift from fossil ethylene to (bio)ethylene will always bring environmental gains, independent of how much iLUC may occur. On the other hand, the category *ecosystems* showed positive results in scenarios A and B, and negative in scenario C; and its magnitude was highly dependent on the iLUC scenarios. This means that the shift from fossil ethylene to (bio)ethylene will increase impacts on ecosystems up to a certain degree of iLUC, being possible to reach high values (up to 4.2E+02 higher at scenario A). The threshold for environmental gains was approximately 0.2%, meaning that the shift from fossil ethylene to (bio)ethylene will reduce ecosystem impacts as long as the iLUC is lower than 0.2% of the area of sugarcane cultivated (Figure 5.4a). The main reason for these results were due to the impacts on biodiversity caused by the iLUC, since the Recipe Endpoint method does provide characterization factors for land use change, even though they are not spatial-differentiated (contrary to the method from de Baan et al. (2012). Meanwhile, the category *human health* was also sensitive for the degree of iLUC, producing increased environmental impacts at scenario A, but environmental gains in scenarios B and C. The threshold for the environmental gains was approximately 24.9% (Figure 5.4b).

From Table 5.6 we can see that for the single score results, scenarios A and B generated positive values, i.e., increased environmental impacts, and Scenario C generated negative results, i.e., environmental gains. The threshold for the environmental gains was approximately 5.7%, i.e., (bio)ethylene results in overall environmental gains if iLUC is lower than 5.7% of the area of sugarcane cultivated (Figure 5.4c).

Table 5.6: Results for the consequential approach of 1 kg of bioethanol-based PVC resin, at endpoint level, with the respective values of coefficient of variation (C.V.)

Endpoint category / Single score	Unit	Scenario A Mean value	Scenario A C.V.	Scenario B Mean value	Scenario B C.V.	Scenario C Mean value	Scenario C C.V.
Resources	Dollars ($)	-1.32E+01	2%	-1.32E+01	1%	-1.32E+01	1%
Human health	DALY	2.92E-06	56%	-4.63E-07	62%	-9.68E-07	23%
Ecosystems	Species.yr	5.56E-06	40%	7.12E-07	35%	-1.31E-08	59%
Single score	Ecopoints (Pt)	2.56E+00	41%	1.98E-01	55%	-1.54E-01	6%

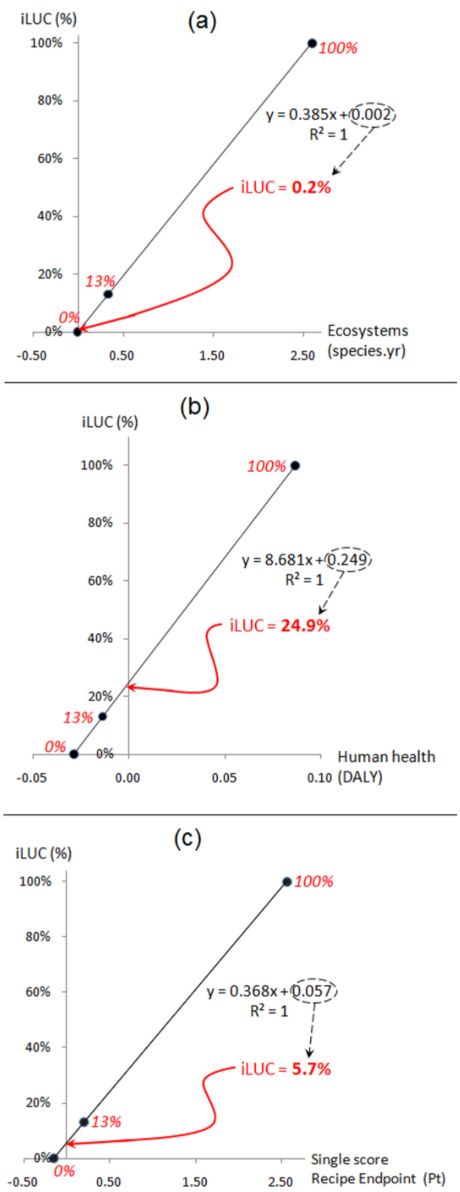

Figure 5.4: Correlation of the scenarios of iLUC with the potential environmental impact at endpoint ecosystem (a), endpoint human health (b), and at endpoint single score results (c), for 1 kg of PVC resin

5.3.3 Outlook

In the last section we were able to estimate thresholds for iLUC factors where bioethanol-based PVC would still produce better results than fossil-based PVC. If we look to historical data on dLUC in Brazil between 2003 and 2009 (FAO, 2012), we can see that while forested areas decreased 180,000 km^2, the overall expansion of agricultural area (i.e., arable land, permanent crops, and pasture land) was 9,000 km^2. Literature suggests that the relationship between the expansion of agricultural area and the reduction of forested area is driven by dLUC from soybeans, timber, and cattle, rather than by iLUC from sugarcane (Harvey and Pilgrim, 2011; Nassar et al., 2008). It is known that dLUC can be accurately quantified, while accounting for iLUC from a specific product (as bioethanol) present many uncertainties (Adami et al., 2012; Sparovek et al., 2009). On the other hand, some studies suggested a correlation between deforestation and iLUC from sugarcane expansion (Lapola et al., 2010). Based on these, we provided some hard numbers to this discussion, considering a range of iLUC factors from 0% to 100%. This study allowed us to evaluate how the conclusions obtained in the attributional LCA (Alvarenga et al., 2013a) could change by the inclusion of iLUC (through consequential LCA). For instance, while at the endpoint analysis of the attributional LCA the bioethanol-based PVC (scenario from 2018) had better results than fossil-based PVC for the aggregated single score results, in the consequential LCA we could notice that this conclusion was limited to a certain relative iLUC factor, i.e. 5.7%.

5.4 CONCLUSIONS

Whereas the iLUC studied in this paper did not affect all environmental impact categories when shifting from fossil ethylene to (bio)ethylene, at midpoint level the shift did generate environmental gains at the categories *non-renewable resources*, *ionizing radiation*, and *climate change* (significant for scenarios B and C). At endpoint level, this shift of feedstock would produce environmental gains for the category *resources*, but also for the category *ecosystems* and *human health*, as long as the iLUC was not higher than 0.2% and 24.9%, respectively, and for the aggregated single score results, as long as iLUC was not higher than 5.7%.

The effects of iLUC appeared to be important, and should be considered when assessing new bio-based products. Even though iLUC is based on assumptions for the future, therefore with high uncertainties, the results showed in this paper were important to highlight the importance of information on the area affected by iLUC due to new bio-based products, and to provide quantitative results to the stakeholders showing that some environmental gains may be nullified if there is low control on deforestation caused by iLUC.

CHAPTER 6: Plastic vs. fuel: Which use of the Brazilian ethanol can bring more environmental gains?‡‡‡

ABSTRACT

Ethanol from sugarcane is mainly used as fuel for cars in Brazil. However, the chemical industry is considering ethanol also as biotic feedstock for several plastics (e.g. polyethylene and polyvinyl chloride). Both uses are able to cause less environmental impacts than their fossil references if we look to certain specific environmental impact categories such as fossil energy consumption and greenhouse gas (GHG) emissions. However, which use would be able to bring the most environmental gains to society? In order to answer this question, we performed an attributional life cycle assessment of using 1 kg of hydrous ethanol as fuel for transportation and the same amount for monomer production (ethylene), and compared them with the common practice of today in Brazil. Using ethanol to produce ethylene (instead of fossil-based ethylene) would generate environmental gains in the order of 32.0 MJ of fossil energy and 1.87 kg CO_2eq, whereas the use of ethanol for transportation (instead of gasoline mixture, for flex-fuel cars) would generate environmental gains in the order of 27.2 MJ of fossil energy and 1.82 kg CO_2eq. Some uncertainties were quantified, for instance we could observe that when the ethanol-to-ethylene reaction yield was lower than 96%, the fuel route had better results for GHG emission savings.

Keywords: Ethanol, Ethylene, Fuel, Life cycle assessment

6.1 INTRODUCTION

Ethanol can be produced from several types of biomass, but in Brazil it is mainly produced from sugarcane. The sugarcane-ethanol industry in Brazil has already shown good performance, reaching energy ratios of 9.3 (Macedo et al., 2008), i.e., for every 1 MJ of fossil energy supplied, 9.3 MJ of bioenergy is provided. Ethanol (from sugarcane) is the source of biofuels in Brazil since the 1970’s (Goldemberg et al., 2008), either as stand-alone fuel (E100) or blended with gasoline (e.g. E25). In the last years it has also been (re)considered as an alternative for making renewable plastics, for instance to produce bioethylene for

‡‡‡ Redrafted from: Alvarenga, R.A.F; Dewulf, J. 2013. Which use of the Brazilian ethanol can bring more environmental gains? *Renewable Energy*, v. 59, pp 49-52.

polyethylene (Braskem - http://www.chemicals-technology.com/projects/braskem-ethanol/), for polyvinyl chloride (Solvay S.A. - http://www.plasticstoday.com/articles/solvay-indupa-invests-sugar-cane-derived-ethylene-pvc), and for polyethylene terephthalate (The coca-cola company - http://www.thecoca-colacompany.com/citizenship/plantbottle.html). Ethanol has several other applications (e.g. pharmaceutical), but considering the established biofuel market in Brazil and the potential increase in the bio-based plastics market (Reisch, 2012), these two uses are the most promising.

When hydrous ethanol (with 96° GL) is used as fuel for cars in Brazil (100), it avoids the use of gasoline mixture, which includes typically 20-25% (in volume) of anhydrous ethanol (with 99.7° GL) (Brazilian law number 10.203, from 2001). At the same time, when hydrous ethanol is used to produce bio-based ethylene, fossil-based ethylene is avoided. In this sense, we may raise the question of which of these two uses for hydrous ethanol may bring more benefits to the environment? The objective of this study was to evaluate which of the two options for using hydrous ethanol (as fuel for cars or as monomer in the chemical industry) could bring more environmental gains to society. Since most of the studies that compared bio-based and fossil-based fuels/plastics have shown that the contributions are mainly in the decrease of greenhouse gases (GHG) emissions and fossil energy consumption (Alvarenga et al., 2013a; Cavalett et al., 2013; Liptow and Tillman, 2012), we focused on these two environmental impact categories.

6.2 MATERIAL AND METHODS

We used attributional life cycle assessment (LCA) methodology, but unlike traditional LCA studies which assess two or more comparable products, we assessed the environmental impacts of two different possible uses for hydrous ethanol. Consequently, in order to have comparable results between these two possibilities, we subtracted from the results the value of the alternative products that ought to be used in Brazil (Figure 6.1), i.e., the fossil-based ethylene and the gasoline mixture E22 (petrol with addition of anhydrous ethanol). The functional unit chosen was 1 kg of ethanol.

The sugarcane and ethanol production processes and supply chain were considered the same for both routes, based on data from Cavalett et al. (2013). According to them, 1000 kg of sugarcane (which requires approximately 120 m^2.year of land use) can produce 69.3 kg of hydrous ethanol. At the ethanol production process, electricity is co-produced, and in order to avoid allocation (ISO, 2006b), we performed a *system expansion* with the Brazilian electric grid, based on data from the ecoinvent database (Ecoinvent, 2010).

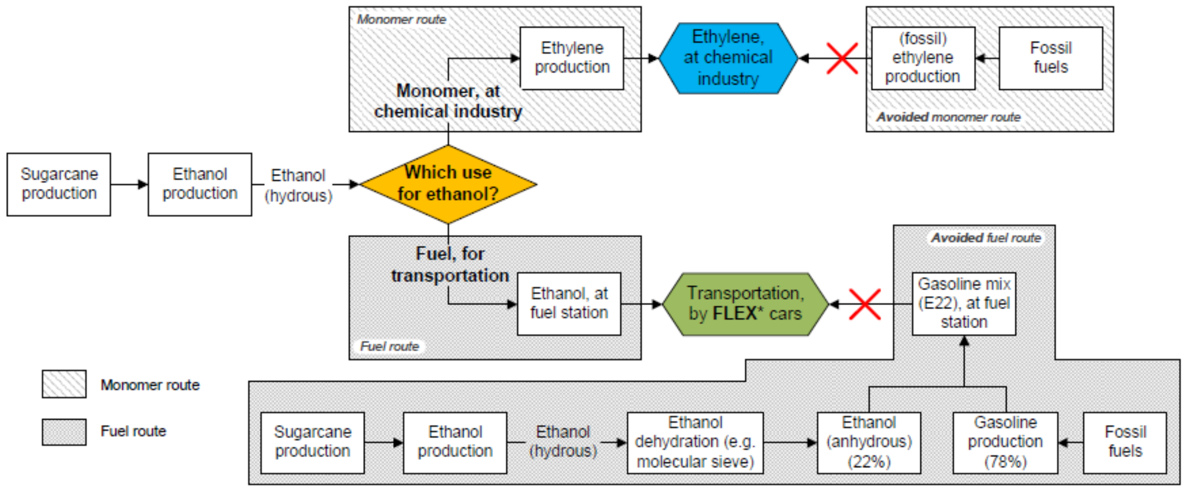

Figure 6.1: Simplified flowchart of the two possible uses for hydrous ethanol considered in this study

In the monomer route, the ethylene production process was based on data from the CPM LCA Database (CPM, 2008), where a reaction yield of 100% is assumed. In this sense, for the functional unit of 1 kg of ethanol, 0.588 kg of bioethylene would be produced, which was used as the reference flow for the monomer route. The bioethylene produced may be used for different purposes (e.g. polyethylene), but we stopped our analysis at the monomer since the bio-based ethylene monomer has the same technical qualities of the fossil-based. For the fossil-based ethylene avoided we used the process 'Ethylene, average, at plant/RER', from the ecoinvent database (Ecoinvent, 2010).

In the fuel route, we considered that ethanol would be used in a flex-fuel car (Palio fire 1.0), with average fuel consumption of 10 L/100km (for hydrous ethanol – E100) or 7.04 L/100 km (for gasoline with 22% of anhydrous ethanol – E22). Therefore, for our functional unit of 1 kg of ethanol, the reference flow at the fuel route was 12.7 km. The gasoline mixture (E22) avoided was modeled using the process 'Petrol, low-sulphur, at refinery/RER', from ecoinvent database (Ecoinvent, 2010) and the anhydrous ethanol production from Cavalett et al. (2013). The atmospheric emissions from the combustion of the fuels (at the use phase) were based on vehicle emission reports from *Companhia de Tecnologia de Saneamento Ambiental* (CETESB), the environmental agency from the state of Sao Paulo (Brazil) (CETESB, 2004).

For the life cycle impact assessment stage, we used the fossil category of the method *Cumulative Energy Demand* (Hischier et al., 2009), to calculate the fossil energy demand of each product; and the method IPCC 2007 (100 years) (IPCC, 2007), to evaluate the GHG emissions. For the latter, we also considered carbon dioxide absorption and biogenic emissions.

This study is sensitive to several sources of uncertainties; two of them were quantified and are presented together with the results. First, while the reaction yield of ethylene produced from hydrous ethanol in the CPM LCA Database (CPM, 2008) was 100%, Alvarenga et al. (2013a) mentioned a reaction yield of approximately 90% (which would produce 0.53 kg of ethylene per kg of ethanol, instead of 0.588 kg). The second source was regarding the blend of anhydrous ethanol in the Brazilian gasoline mixture. According to Federal law (Brazilian law n° 10.203, from 2001), 22% of anhydrous ethanol should be blended to the gasoline mixture (E22), however this value changed throughout the years, for political and economical reasons, varying from 20% (E20) to 25% (E25).

6.3 RESULTS AND DISCUSSION

6.3.1 Environmental profiles

In Table 6.1 we present the GHG emission and fossil energy consumption for the production of the bio-based products and the fossil-based products that can be substituted. Second, in case of fuel applications, emissions at the use phase were calculated as well.

Table 6.1: GHG emissions and fossil energy consumption throughout the life cycle of the different products (values are per kilogram of product) [(a)]

Life cycle phase	Product		GHG emissions (kg CO_2eq / kg)	Fossil energy consumption (MJ $_{fossil}$ / kg)
Production phase (*cradle-to-gate*)	Hydrous ethanol	Bio-based (E100)	-1.55	2.00
	Gasoline mixture	E20 (20% bio-based)	0.17	44.10
		E22 (22% bio-based)	0.13	43.10
		E25 (25% bio-based)	0.06	41.50
	Ethylene	Bio-based (w/ reaction yield of 100%)	-1.78	10.79
		Bio-based (w/ reaction yield of 90%)	-1.62	12.00
		Fossil-based	1.40	65.20
Use phase	Hydrous ethanol	Bio-based (E100)	1.76	-
	Gasoline mixture	E20 (20% bio-based), E22 (22% bio-based), E25 (25% bio-based)	2.86	-

(a) Positive values mean GHG emission and fossil energy consumption, while negative values for the GHG emissions mean that the absorption of CO_2 is higher than the overall emissions of GHG

6.3.2 Fossil energy consumption savings

From the values from Table 1 we can see that when considering a reaction yield of 100% for ethylene produced from hydrous ethanol, 0.588 kg of (bio)ethylene has a cumulative fossil energy demand of 6.34 MJ. This product avoids the cumulative consumption of 38.34 MJ of fossil energy from the fossil-based ethylene, leading to a net fossil energy saving of 32.00 MJ (Figure 6.2). However, when we considered a reaction yield of 90%, the net fossil energy saving was lower (28.20 MJ). In the fuel route, the transportation of 12.7 km led to a cumulative fossil energy demand of 2.00 MJ for hydrous ethanol (E100), while for the gasoline mixture (E22) the cumulative fossil energy consumption was 29.20 MJ (for 12.7 km it is needed approximately 0.68 kg of E22 or 1 kg of hydrous ethanol), leading to a net fossil energy saving of 27.20 MJ (Figure 6.2). When hydrous ethanol replaced gasoline E20, a higher energy saving was observed (27.90 MJ), but when the same fuel would replace gasoline E25, a lower energy saving was observed (26.10 MJ). Overall we could see that the monomer route had better results for fossil energy savings, even when the reaction yield of ethylene was 90%. In fact, the ethanol-to-ethylene reaction yield should be lower than 89% in order to the fuel route have better results than the monomer route (considering E100 replacing E20).

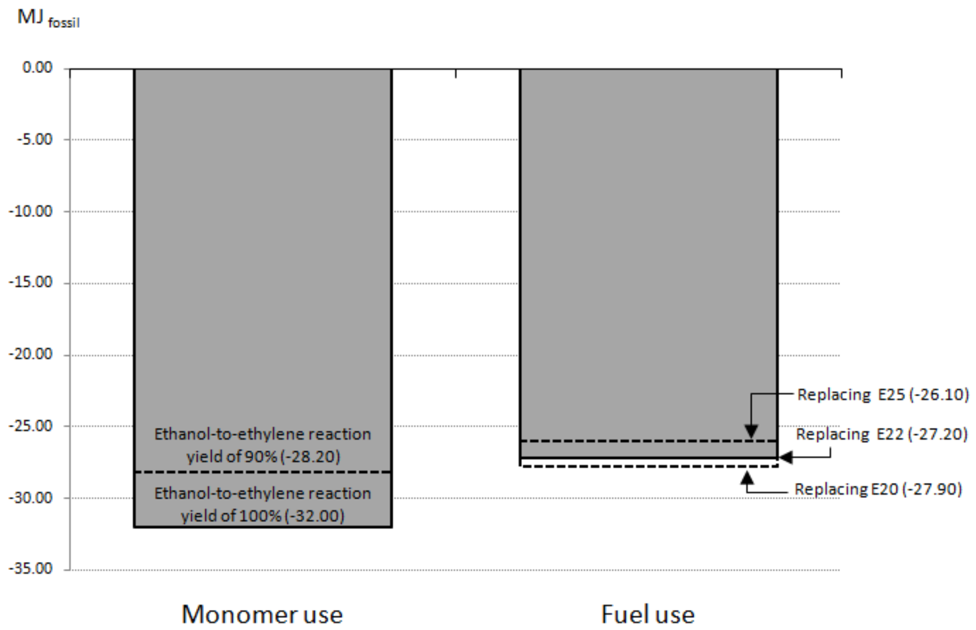

Figure 6.2: Fossil energy savings when using hydrous ethanol as monomer (left) or as fuel for transportation (right) in comparison to the Brazilian benchmarks

6.3.3 Greenhouse gas (GHG) savings

Even though the production of ethanol has GHG emissions in several sub-processes (e.g. sugarcane harvest), it had a negative value of 1.55 kg CO_2eq, since the carbon present in this chemical was previously absorbed by the sugarcane plant. For the monomer route, (bio)ethylene had a cumulative GHG emission of –1.05 kg CO_2eq, with a reaction yield of 100% (therefore 0.588 kg of ethylene produced), while the fossil-based ethylene had a cumulative GHG emission of 0.82 kg CO_2eq. These values led to a net GHG saving of 1.87 kg CO_2eq, since the fossil ethylene would be avoided (Figure 6.3). With a reaction yield of 90%, the net GHG savings would decrease to 1.60 kg CO_2eq. For the fuel route, the combustion of hydrous ethanol (E100) at the use phase emitted 1.76 kg CO_2eq, making the carbon footprint of hydrous ethanol in cradle-to-grave analysis equal to 0.21 kg CO_2eq. On the other hand, the cradle-to-grave carbon footprint of the gasoline mixture (E22) was equal to 2.03 kg CO_2eq, with approximately 1.94 kg CO_2eq from the use phase. This led to a GHG saving of 1.82 kg CO_2eq, if pure ethanol is used instead of gasoline mixture (E22), for transportation over 12.7 km. Lower GHG emissions savings were observed when pure hydrous ethanol replaced gasoline E25 (1.77 kg CO_2eq), and the opposite when the replacement considered was E20 (1.85 kg CO_2eq). Overall the monomer had better results than the fuel route, as long as the ethanol-to-ethylene reaction yield was 100%. The fuel route would have better results than monomer route (for the three blends considered in this study) if the ethanol-to-ethylene reaction yield would be lower than 96%.

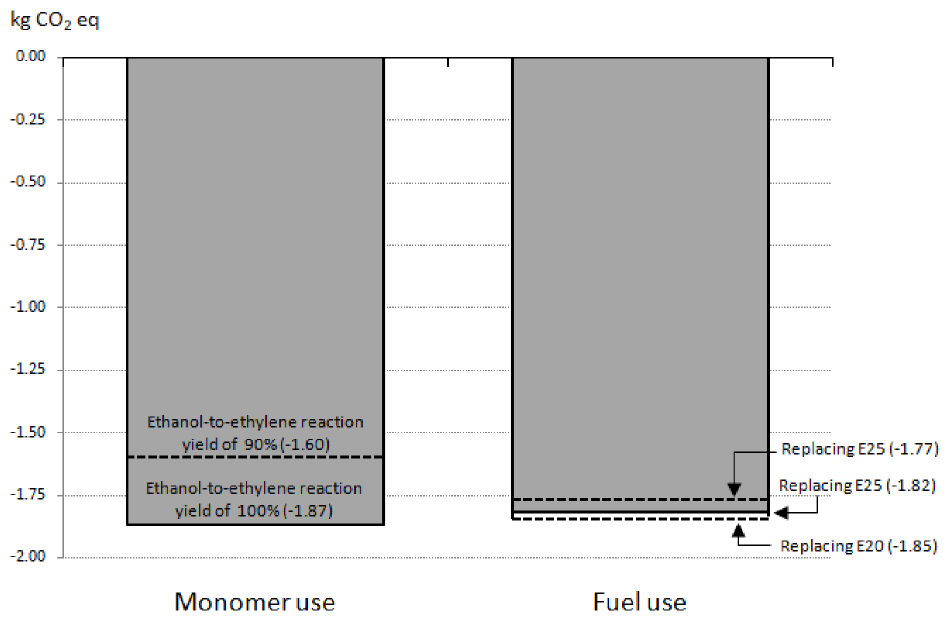

Figure 6.3: GHG savings when using hydrous ethanol as monomer (left) or as fuel for transportation (right) in comparison to the Brazilian benchmarks

6.4 CONCLUSIONS

In this study we analyzed which use of sugarcane-based hydrous ethanol (to produce a monomer or to be used as fuel) would bring more environmental gains to society through attributional LCA. We could see that both uses indeed cause environmental gains at fossil energy consumption and GHG emissions, when compared to the common practice of today in Brazil. However, the use of hydrous ethanol for monomer production in the chemical industry appeared to cause higher fossil energy and GHG emission savings, as long as the ethanol-to-ethylene reaction yield was 100%.

The results of this study are subject to several sources of uncertainties. Two of them were quantified, and we could observe shifts on the results, e.g., the fuel route could have higher savings for GHG emissions if the ethanol-to-ethylene reaction yield would be below 96%. Apart from those, other sources of uncertainties could affect the results, as (a) higher/lower electricity co-produced with the ethanol, since different values are observed in different literature sources (Macedo et al., 2008; Macedo et al., 2004; Seabra et al., 2011); (b) using allocation (based on energy or economic values) instead of system expansion for the electricity co-produced; (c) different allocation methodologies used in the fossil ethylene and petrol production, instead of what was chosen in ecoinvent database; and (d) other more traditional sources of uncertainties in LCA, as the data collection and the impact assessment methods. It is also important to emphasize that the results shown in this paper are based on secondary data from different sources, and in order to draw more concrete conclusions, it would be desirable to perform the same study with primary data (at least for the foreground processes), which can be considered as future challenges left by this paper.

On top of that, these results may be also questioned regarding possible rebound effects of environmental impacts. For instance, ethanol to fuel is already well established in Brazil, and if part of it would change to monomer route, it would either cause expansion of sugarcane fields for more ethanol production, possibly causing indirect land use change (iLUC) impacts, (which are the impacts from the land use change occurring outside of the product's boundaries), or importation from other countries (e.g. United States of America), since the demand of hydrous ethanol to fuel would still exist. On the other hand, it may be considered that ethanol to monomer is a recent market, and the origin of it would be exclusively from new sugarcane areas, making them totally responsible for iLUC impacts. However, our study was performed through attributional LCA, and we would like to leave these questions as future challenges, to be considered in a consequential approach.

CHAPTER 7: Conclusions and Perspectives

This PhD Dissertation was divided in two research issues. In the methodological issue (chapters 2 and 3), scientific advances were proposed in order to assess biobased products in a more consistent way. Regarding the applied issue of this PhD Dissertation, in chapters 4 and 5 we performed the life cycle assessment (LCA) of bioethanol-based PVC through attributional and consequential approaches, and in chapter 6 we analyzed which use of bioethanol would bring more environmental gains to society, considering the currently reality of Brazil.

7.1 CONCLUSIONS AND GENERAL DISCUSSION

In chapter 2 we introduced a new accounting method for land resources in exergy terms, to be used in LCA. The starting point of this method is the clear definition of its system boundaries, creating two different approaches: (1) one for natural systems, based on the exergy value of the biotic resource extracted; and (2) another for human-made systems, based on the land that is deprived from nature and/or that competes with other human uses. The approach for human-made systems, based on the potential net primary production (NPP), uses data from Haberl et al. (2007) and therefore is able to generate spatial-differentiated characterization factors. In this chapter, spatial-differentiated data were made available at continent level, country level, state level (for the 6 largest countries in the World), and at grid level (in which visualization is available only through GIS software). When tested into case studies, the new method generated different results in comparison to more traditional RAM (CED, CExD, and CEENE). However, it is scientifically not possible to set which of these methods are the best, since each one has its own assumptions and approaches. Nevertheless, the method proposed in chapter 2 has the advantage of combining the approach from CED and CExD (for natural systems) with the approach from CEENE (for human-made systems). When the method proposed in chapter 2 was coupled with the CEENE method, the importance of spatial-differentiated characterization factors could be highlighted through case studies, showing results for overall resource accounting up to 77% higher.

If results from chapter 2 are implemented with other exergy-based RAM (or even energy-based RAM), the issue of pressure on land could be dealt in a better way. Currently, certain RAM (as CED or CExD) account for land resources through the energy (or exergy) content, which is rather an energetic point of view than an environmental point of view, as the pressure on land is overlooked. Other RAM that already deal with land use (e.g. CEENE), could gain precision if implementing the results from Chapter 2, due to the spatial differentiation of land (in exergy terms).

In chapter 3 we made use of the results from the previous chapter to elaborate a new indicator for the natural resource balance of land use systems (ΔEP). It was tested in several agricultural case studies and the results showed that, through a life cycle perspective, this new indicator was able to fill some gaps of two well-established resource balance indicators from literature: the net energy value and the method from Haberl et al. (2007) (ΔNPP_{LC} or HANPP). The ΔEP appears to be more holistic than the previous two, since it takes into account the biomass produced, the land deprived, and the overall non-local resources consumed/used.

When implemented into an exergy-based RAM, the results from chapter 2 can be used for all types of products (biobased or not). On the other hand, the indicator proposed in chapter 3 (ΔEP), which is actually an outcome of the results from chapter 2, may be used solely for terrestrial biomass production (and other land-based exergy productions, as solar exergy). This means that its application is limited to the farm/forest gate. For instance, if it would be applied to the bioethanol-based PVC (chapters 4 and 5), up to the farm gate the results would be very similar from CS2 of chapter 3, but when going downstream (i.e., bioethanol, (bio)ethylene, and PVC production stages), it would produce results not different from traditional cumulative exergy analysis.

In chapter 4 we analyzed the environmental sustainability of bioethanol-based polyvinyl chloride (PVC), through LCA. In this study we made use of the method created in chapter 2, but also of other midpoint LCIA methods and an endpoint LCIA methodology (Recipe Endpoint H/A). From the results obtained, we could see that when shifting from a fossil-based to a biobased source of raw material, the environmental impacts of PVC on resource depletion and climate change would decrease, but on the costs of other environmental impacts (e.g. biodiversity). Nevertheless, when using the single score of the Recipe Endpoint H/A method, bioethanol-based PVC had up to 1/3 of the overall environmental impacts of the fossil-based PVC.

In chapter 5 we showed that the conclusions of chapter 4 should be interpreted with care, since different conclusions may be obtained when the effects of indirect land use change (iLUC) are considered. The methodologies to evaluate iLUC caused by a certain product are still on debate, as well as its inclusion in LCA. Yet, in our study we concluded that bioethanol-based PVC still appears to be a better option than fossil-based PVC, from an environmental sustainability perspective, when the degree of iLUC is lower than a certain percentage of the sugarcane cultivation area (e.g. 5.7% for the single score of the Recipe Endpoint H/A).

Water use is considered to be a critical aspect in LCA of biobased products, together with land use (soil degradation and biodiversity) and carbon storage (Pawelzik et al., 2013). In the study of the bioethanol-based PVC (chapters 4 and 5), the water use was considered in a rather simple way, using the CEENE method for midpoint analysis and without an impact assessment method at the endpoint analysis, since water use is not addressed in the Recipe Endpoint methodology. Recently some new LCIA methods were introduced, dealing with water consumption, as the method from Milà i Canals et al. (2009) dealing with the environmental impacts in two AoP (resources and natural ecosystems), and the method from Pfister et al. (2009) dealing with the environmental impacts in three AoP (natural resources, natural ecosystem, and human health). The former is qualified by its authors as providing midpoint indicators, while the latter as providing both midpoint and endpoint indicators. In this sense, one of these two LCIA methods could have been used in the study of bioethanol-based PVC at midpoint level, in substitution to the CEENE method. At endpoint level, the implementation of the method from Pfister et al. (2009) would have been more difficult, since the characterization factors are not in the same units of the Recipe Methodology. For instance, in the Recipe Endpoint methodology the units for natural environment are *species.year*, while in Pfister et al. (2009) the units are $PDF{*}m^2year$. This is a relevant issue since the endpoint analysis of the bioethanol-based PVC was performed at the aggregated results of the AoP (Table 4.4) and at the single score level (Figure 4.3). Nevertheless, it is important to mention that the sugarcane cultivation system considered in the study was without irrigation, therefore there was no direct consumption of (blue) water in the agricultural phase (Table 10.19). The water consumption at the bioethanol production phase (Table 10.20), responsible for approximately 80% of the overall water consumption of the bioethanol-based PVC, may be considered as rather low (58 L/L ethanol for scenario 2010 and 42 L/L ethanol for scenario 2018) when compared with the consumption of other biofuels. For instance in Harto et al. (2010), corn-based ethanol is classified as 'low water use' (28 L/L ethanol), 'average water use' (138 L/L ethanol), and 'high water use' (423 L/L ethanol) (all values of water consumption per volume of ethanol are after performing allocation).

Climate change is one of the main drivers for production of biobased products and, therefore, it is a very important aspect when assessing their environmental sustainability. The method IPCC 2007 (100 years) is the most recommended for LCA studies (European Commission, 2011b; Hauschild et al., 2013), which was used in our assessments in chapter 4, 5, and 6. However, this method does not deal with biogenic emissions in a proper manner, and some research has been done to tackle this scientific gap. Recently, characterization factors for global warming potential of biogenic carbon dioxide emissions (GWP_{bio}) have been developed in Cherubini et al. (2011), which are in function of the time period of crop rotation, i.e., the longer the crop rotation, the longer the biogenic CO_2 will stay in the atmosphere, and therefore, the higher the GWP_{bio}. Based on that method, GWP_{bio} for carbon stored in biobased products were developed in Guest et al. (2012), in which they are in function of time period of the crop rotation and also in function of the carbon storage time in the final product. In this sense, if we would have used the methods from Cherubini et al. (2011) and Guest et al. (2012) in the studies from chapter 4, 5, and 6, in addition to the IPCC 2007 (100 years), some differences might have occurred in the final results. Nevertheless, due to the characteristics of the two former methods, the LCA could not have been done in a cradle-to-gate approach, i.e., it would have to account also for the carbon emissions occurring in the downstream processes, for instance, the carbon emissions of the incineration of the PVC (after some years, depending on the final use of the PVC).

To give a better ground for this discussion, the methods from Cherubini et al. (2011) and Guest et al. (2012) were applied in this section to the carbon dioxide emissions from the study done in chapter 4, but including also the downstream emissions (assuming that the PVC product would be incinerated). It is important to know the life-time of final product. PVC products are usually designed to last for more than 50 years (up to 100 years), and in many times they are only replaced earlier due to physical damages or esthetics issues (e.g. window frame). For this section a storage time of 50 years was assumed, but this number can be debated. Additionally, the GWP_{bio} of the biogenic carbon emissions occurring during the production of the bioethanol-based PVC (e.g. CO_2 released during fermentation of ethanol) is different from the GWP_{bio} of the emissions of the biogenic carbon stored in the product and later released during incineration. For the former, the value used (for 1 year of crop rotation) was 0.00 $kgCO_2eq/kg$ (Cherubini et al., 2011) and for the latter the value used (for 1 year of crop rotation and storage time of 50 years) was -0.40 $kgCO_2eq/kg$ (Guest et al., 2012). The results for the climate change potential impact of bioethanol-based PVC (scenarios of 2010 and 2018) and fossil-based PVC, using the methods from Cherubini et al. (2011) and Guest et al. (2012), in addition to the method IPCC 2007 (100 years), can be seen in Table 7.1. It is important to mention that 0.384 kilogram of carbon is present in one kilogram of PVC resin, which is equivalent to an emission factor of 1.41 kg of CO_2 per kilogram of PVC resin, and that the emission factor of fossil CO_2 is equal to 1.00 $kgCO_2eq/kg$.

Table 7.1: Possible different values in Climate Change of the attributional life cycle assessment study of 1 kg of bioethanol-based PVC if the methods from Cherubini et al (2011) and Guest et al. (2012) were also used

Climate change (kg CO_2 eq.)	Bioethanol-based PVC (2010)	Bioethanol-based PVC (2018)	Fossil-based PVC (2010)
Uptake of CO_2	0.00	0.00	0.00
Biogenic emissions	0.21	0.09	0.05
Fossil emissions	1.12	1.06	1.36
CO_2 emissions due to dLUC	0.16	0.15	0.10
Emissions at downstream (e.g. incineration of PVC)	-0.56	-0.56	1.41
Total net emissions	0.93	0.74	2.92
Value of total net emissions used in the original study (Table 10.23), but adjusted for a cradle-to-grave analysis (considering GWP_{bio} = 1)	1.32	1.22	2.92

In order to avoid double-counting, the uptake of CO_2 should not be accounted (Cherubini, personal communication). The biogenic emissions of CO_2 are equal to zero due to the GWP_{bio} of same number, and the values in the row 'biogenic emissions' in Table 7.1 are related to biogenic carbon monoxide and methane emissions. The values for fossil emissions and CO_2 emissions due to direct land use change are kept the same. The additional issue is the accounting of carbon emissions downstream. For the bioethanol-based PVC, the carbon emitted is biogenic, therefore GWP_{bio} equal to -0.40 $kgCO_2eq/kg$, while for the fossil-based PVC, the carbon emitted is fossil, so the global warming potential is equal to 1 $kgCO_2eq./kg$. This is the reason why the values in the row of the emissions downstream differ between the bioethanol-based PVC (-0.40 $kgCO_2eq/kg \times 1.41$ kg = -0.56 $kgCO_2eq$) and the fossil-based PVC (1.00 $kgCO_2eq/kg \times 1.41$ kg = 1.41 $kgCO_2eq$), even though the amount of CO_2 emitted is the same (1.41 kg). When the values from Table 10.23 (from the original study of chapter 4) are adapted to account also for the downstream emissions (during incineration), the results are 1.32, 1.22, and 2.92 $kgCO_2eq/kg$, for bioethanol-based PVC (2010), bioethanol-based PVC (2018), and fossil-based PVC, respectively. On the other hand, if the methods from Cherubini et al (2011) and Guest et al. (2012) would have been implemented in addition to the method IPCC 2007 (100 years), the total net emissions would be 0.93, 0.74, and 2.92 $kgCO_2eq/kg$, for bioethanol-based PVC (2010), bioethanol-based PVC (2018), and fossil-based PVC, respectively. For the bioethanol-based PVC these new values are 70% (2010) and

60% (2018) of their original value (adjusted to downstream emissions). Therefore, it can be concluded that the climate change potential impact of the bioethanol-based PVC could be even lower, if used more recent LCIA methods, as Cherubini et al (2011) and Guest et al. (2012).

These new LCIA methods for Climate Change impacts of biogenic CO_2 bring new interesting discussions to biobased products (e.g. bioethanol-based PVC). For instance, by simply using the IPCC 2007 (100 years), the emissions of biogenic CO_2 stored in biobased products would have the same global warming potential regardless the type of biobased feedstock. On the other hand, when the new LCIA methods from Cherubini and colleagues are used, this conclusion can differ: the biogenic CO_2 emitted from biobased products produced from bioethanol from sugarcane (one year of rotation cycle) has lower GWP_{bio} than the biogenic CO_2 emitted from biobased products produced from bioethanol from wood (Liptow et al., 2013), which has a longer rotation cycle.

The environmental sustainability of the bioethanol-based polyethylene (PE) was assessed in Liptow and Tillman (2012), in which Brazilian sugarcane was used as feedstock, and it was compared with fossil-based PE. Therefore, even though it is not bioethanol-based PVC (studied in chapters 4 and 5), the sugarcane, bioethanol, and ethylene production stages can be compared with this PhD Dissertation. They used five environmental impact categories for the LCA study: Climate change, primary energy use, acidification potential (AP), eutrophication potential (EP), and photochemical ozone creation potential (POCP). The results for primary energy use, climate change, and eutrophication potential were similar to the results obtained in chapters 4 and 5, i.e., sugarcane-based (bio)ethylene had lower consumption of non-renewable energy (and higher consumption of renewable energy), lower climate change impacts (depending on the level of emissions from iLUC) and higher EP. However, the results for POCP and AP were different: sugarcane-based (bio)ethylene had lower impacts than fossil-based ethylene in Liptow and Tillman (2012), while the opposite was observed in the study from chapters 4 and 5. Most likely, the main reason for that is at the life cycle inventory (LCI) phase: Several gases emitted at the sugarcane cultivation stage were not accounted in the study from Liptow and Tillman (2012). While in that stage they considered solely emissions of CH_4 and N_2O, in our study we considered also the emissions of NMVOC and CO (that contribute to POCP), NH_3 (that contribute to AP), and SO_X and NO_X (that contribute to POCP and AP). Besides, emissions of particulate matter (especially during the manual harvest) were not accounted, which in the study of chapters 4 and 5 showed an important contribution to the final single score (aggregated) results. On top of that, the ethanol-to-ethylene ratio considered in Liptow and Tillman (2012) was 1.70 while in our study it was considered to be 1.88. This means that in our study more bioethanol (and therefore more sugarcane) was needed to produce the same amount of ethylene.

There have been some discussions in the scientific community over the best approach when conducting a LCA study, either attributional or consequential, somehow creating two schools of thoughts. However, while conducting the study from chapter 5, it was concluded that a *pure* consequential LCA is not yet feasible. For instance, literature suggests that marginal data should be used in a consequential LCA, but, as in any other type of LCA study, background data are needed, which are usually provided by LCI databases (e.g. ecoinvent database). The issue is that these LCI databases often make use of average data, and not marginal data. Thus, when making a consequential LCA which makes use of LCI databases, marginal data might be used for the foreground data, but average data will still be used for the background data, making the study rather a *partial* consequential LCA. The example of marginal vs. average data was just illustrative, but there are other characteristics of background LCI databases (which are rather attributional) that still make a *pure* consequential LCA unfeasible (e.g. allocation vs. system expansion). Pawelzik et al. (2013) suggested that for biobased products consequential LCA should be rather used to answer particular questions, as the environmental impacts due to iLUC. This was how the study of the bioethanol-based PVC was performed (chapters 4 and 5), and goes in accordance with the opinion of the author of this PhD Dissertation.

Bioethanol is mainly used in Brazil for fuel, but it has potential to be used as feedstock in the chemical industry (e.g. PVC and PE). In chapter 6 we analyzed which use of the Brazilian bioethanol would bring more environmental gains (in climate change and resource depletion impacts), considering the current reality of Brazil. We could see that the use of bioethanol for monomer production (in the chemical industry) appeared to cause higher fossil energy and GHG emissions savings, as long as the ethanol-to-ethylene reaction yield was 100%.

The comparison over biobased and fossil-based sources of feedstock is highly discussed in literature. In this PhD Dissertation, this is also discussed in chapters 4 and 5, by comparing different sources for PVC production (sugarcane vs. crude oil and natural gas). The study from chapter 6 already took the assumption that biobased feedstock has better results than fossil-based (for climate change and fossil resource use), bringing the discussion a step forward, i.e., evaluating which final use of the biobased feedstock can bring more environmental gains. However, as mentioned in this study, this was to some extent a superficial analysis, rather to bring this discussion to the scientific community than to give final conclusive answers. It is even suggested in that chapter that a similar study should performed, but more profound, e.g. by using primary data.

7.2 PERSPECTIVES

The results obtained from the research developed from chapters 2 to 6 still leave room for future research challenges, which are discussed below. The challenges left by the methodological issues of this PhD Dissertation (chapters 2 and 3) can be also visualized in a schematic representation in Figure 7.1.

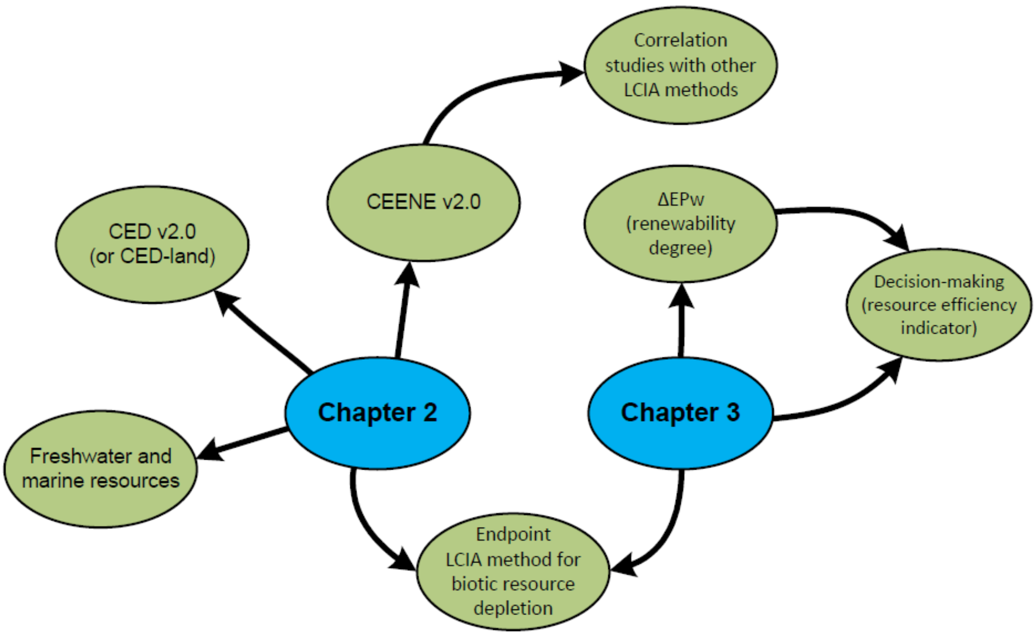

Figure 7.1: Representation of the future challenges left by chapters 2 and 3 of this PhD Dissertation

It is possible to couple the results from chapter 2 into certain RAM. This could first be done with the CEENE method (as it was already performed in section 2.2.3), creating an updated version on that method, so-called CEENE v2.0. In this case, the CEENE v2.0 would differ from the previous version solely regarding the land resources, and would have the following categories: (1) Abiotic renewable resources, (2) Fossil fuels, (3) Nuclear energy, (4) Metal ores, (5) Minerals, (6) Water resources, (7) Land resources, and (8) Atmospheric resources. The characterization factors from chapter 2 would then be used in the category (7).

This could also be done for energy-based RAM, for instance the CED, creating a new version of this method, or even another method (e.g. “CED-land”). Although, this is not as straightforward as in the case of the CEENE method, since the characterization factors from chapter 2 are in exergy values, while the CED method is in energy. Therefore, the first step would be to convert all characterization factors from chapter 2 into energy terms. The simplest way would be to divide them by 1.06, which is considered to be a typical exergy/energy ratio for biomass (as stated in section 2.3.1.1). Further on, the categories “renewable, biomass” and “non-renewable, biomass” (Hischier et al., 2009) would be swapped by a category named “land resources” that would have the results from chapter 2 (but divided by 1.06).

The approach used in chapter 2 is focused on terrestrial land resources, but it could also be applied to ‘marine and freshwater resources’. Therefore, a future challenge is to create spatial-differentiated characterization factors in exergy terms for marine and freshwater resources, i.e., occupation of marine/freshwater areas (in the case of man-made systems, as aquaculture in natural waters) and extraction of marine/freshwater natural biomass (in the case of natural systems, as fishery). It is important to clarify that the method proposed in chapter 2 is already able to account for aquaculture in artificial waters, built on areas that used to be terrestrial land (with the terrestrial natural potential NPP).

The method proposed in chapter 2 can be coupled with certain RAM, as CEENE and CED, as previously mentioned. These RAM are often considered to be a midpoint LCIA method in the resource depletion impact pathway. Although, further research could be done in order to implement the ΔNPP_{LC} indicator from Haberl et al. (2007) as an endpoint LCIA method, which is the change in NPP in a certain area due to land use. The proposed endpoint LCIA method would evaluate the impact from land use on biotic resources in the AoP ‘Natural resources’. In cases where less (or none) biomass is currently produced in a certain land in comparison to its natural potential value ($\Delta NPP_{LC} < 0$), there would be an environmental impact at that AoP (e.g. built-up land use with no biotic production), but when more biomass is produced in comparison to its natural potential value ($\Delta NPP_{LC} > 0$), there would be an environmental gain at the AoP Natural Resources (e.g. sugarcane cultivation in Brazil – as shown in chapter 3). One advantage of this endpoint LCIA method is that it could be spatial-differentiated: Since potential NPP values are already available in that way, the additional work would be to produce site-specific characterization factors for the actual biomass production, which need to be plant-specific as well (e.g. productivity of maize in northern France).

The indicator proposed in chapter 3 (ΔEP) sums the exergy value of different resources in a simple way, regardless the renewability degree of the resource (e.g. metals and biomass). One future challenge left from chapter 3 is to generate weighting factors for different types of resources (e.g. metals), based on their renewability degree. After that, another indicator could be added to the ΔEP (for instance named as ΔEPw), where the sum of the exergy values would be performed after taking into account this weighting factor. For instance, considering a situation where 10 MJ_{ex} of biomass is produced, a NPP_{pot} of 4 MJ_{ex}, and a consumption of 2 MJ_{ex} of fossil fuels and 1 MJ_{ex} of metals, as non-local resources; the result for ΔEP would be +3MJ_{ex}. Although, if there would be certain weighting factors based on renewability degree, the results could be different. Just for illustration, considering arbitrary renewability degree factors of 1, 3, and 2, for biomass, fossils, and metals, respectively, this additional indicator ΔEPw would result in -2MJ_{ex}. This would support a discussion over the use of non-renewable resources for biomass production.

The ΔEP indicator appeared to be more holistic than traditional indicators. Therefore, a future challenge could be the valorization of this indicator to be used in agricultural and forestry studies, promoted by the scientific community and governmental agencies, as an additional indicator to the net energy value. Eventually it could be used, with or without an additional indicator (ΔEPw), as another option for resource efficiency indicator for policy-making (BIO Intelligence Service, 2012), a hot topic at European policy (European Commission, 2011a).

One final perspective regarding the methodological issue of this PhD Dissertation is to elaborate correlation studies between the new CEENE method (‘CEENE v2.0’) and other endpoint LCIA methods. This type of study has been done by Huijbregts et al. (2010) and Huijbregts et al. (2006), but solely for the fossil fraction of the CED. In this way, this study could be used as scientific basis to link the results of the CEENE v2.0 with specific environmental impacts categories (e.g. toxicity and biodiversity loss).

Regarding the applied issue of this PhD, a similar study from chapters 4 and 5 could be done considering social and economic aspects (social-LCA and life cycle costing, respectively), i.e., making a life cycle sustainability assessment (LCSA) (Kloepffer, 2008). In this way, the three pillars of sustainability could be covered. However, LCSA is not yet well-established, mainly due to the social-LCA, which is still on early stages of development, contrary to life cycle costing and (environmental) LCA (Zamagni, 2012). Nevertheless, the social hotspot database (http://socialhotspot.org/) appears to be a good source of data for social-LCA studies, where data for different social indicators (e.g. social equity) can be obtained for different countries and/or different economic sectors (e.g. chemical industry).

Another perspective regarding chapter 5 is to evaluate the consequential LCA of the bioethanol-based PVC considering other iLUC scenarios, for instance: (a) deforestation occurring outside Brazil, induced by the extra demand of Brazilian bioethanol; (b) importation of bioethanol from USA to fulfill the extra demand of bioethanol from Brazil (leading to different direct and indirect environmental impacts); (c) increase in the use of gasoline in Brazil, due to increase in bioethanol prices (causing higher emission of fossil CO and CO_2 and higher use of non-renewable energy, but less emissions of hidrocarbonates, total aldehydes, and NOx (CETESB, 2004)); (d) considering the increase in food prices in addition to LUC impacts, e.g., considering that an extra demand of ethanol in Brazil will cause the importation of ethanol from USA (item b); leading to less available corn for food/feed in USA; leading to the importation of corn from Brazil to the USA; leading to an increase in prices of corn for the internal market in Brazil.

Currently, LCA is mainly used to compare two (or more) products that have the same final use, based on the same functional unit (e.g. transportation of 1 ton of feed by truck or by train). The work done in chapter 6 did not follow this approach, but it compared two different final uses for the same feedstock (bioethanol), through LCA. Bioethanol is not the only biobased intermediate product that might have more than one possible final use, though. In this sense and taking into account the expected increase in biobased products, the creation of a standardized framework for this type of approach should be considered, since it is an unconventional one. Considering a future environmentally sustainable biobased economy, different final uses for biobased (intermediate) products should be analyzed in order to promote those with the best environmental gains.

8. SUMMARY

Certain environmental issues, as climate change and the depletion of fossil fuels, gave support to the renaissance of a biobased economy, where products are to be produced mainly from biomass (so-called *biobased products*). However, biobased products do not automatically mean environmentally sustainable products. In this sense, a proper evaluation of the environmental impacts of biobased products has to be done, through environmental assessment methodologies that consider the life-cycle perspective. In Chapter 1 several environmental assessment methodologies were discussed. Among them, life cycle assessment (LCA) appeared to be the most predominant, but it still has some scientific gaps, as lack of spatial-differentiation and proper evaluation of land use impacts. Other environmental assessment methodologies, so-called resource accounting methodologies (RAM), which are based on the life-cycle perspective and focused on accounting for the cumulative resource used/consumed, appeared to be promising. Nevertheless, they also have specific scientific gaps, as land resource accounting.

In Chapter 2 we introduced a new method to account for land resources through exergy in life cycle assessment. It partitioned the resource accounting methodology in two approaches. For natural systems it was based on the chemical exergy content of the biomass extracted. For human-made systems, it was based on the exergy value of the potential natural net primary production deprived due to human land use. For the latter, spatial-differentiated characterization factors were created. In Chapter 3, the results from Chapter 2 were coupled with a traditional RAM (CEENE), and a new indicator for natural resource balance of terrestrial biomass was created (ΔEP). This indicator was compared to traditional resource balance indicators (e.g. net energy value) through agricultural case studies and presented better results regarding completeness in resources accounting.

In Chapter 4 and 5 the environmental sustainability of bioethanol-based PVC was assessed, through attributional and consequential LCA, respectively. The results of Chapter 4 showed that bioethanol-based PVC has better results than its fossil reference for specific environmental impact categories (climate change and non-renewable resources) and as a single score result (through the LCIA methodology ‘Recipe Endpoint H/A’). In Chapter 5 we included the effects on indirect land use change (iLUC) in the environmental assessment. The results showed that bioethanol-based PVC can still have better results, as long as the iLUC is limited to a certain value, for instance less than 5.7% of the area of sugarcane cultivation. In

Chapter 6 we analyzed the environmental sustainability of two possible uses for the Brazilian ethanol, i.e., as fuel for transportation or as feedstock for the chemical industry (ethylene). The latter appeared to cause more environmental gains for climate change and fossil energy consumption, as long as the ethanol-to-ethylene yield was 100%.

The results of this PhD were able to give contributions to the scientific community in two issues. First, through the creation of new methods and indicators, it was able to fill some scientific gaps of environmental assessment methodologies, mainly regarding spatial-differentiation and land resource accounting. Second, it was able to give information of the environmental sustainability of specific biobased products through LCA. Nevertheless, these results left opportunities for future challenges, discussed in chapter 7.

9. CURRICULUM VITAE

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2008 - 2010 Master in Environmental Engineering (*Mestrado em Engenharia Ambiental*).
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Title of Master thesis (translated): "Evaluation of LCIA methods: a case study of four broiler feed production scenarios"
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2002 - 2006 Bachelor in Environmental and Sanitation Engineering (*Engenharia Sanitária e Ambiental*).
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2000 - 2001 High school, North Posey High School – Poseyville (Indiana), U.S.A.
1998 - 2000 High school, Centro Educacional Leonardo da Vinci – Brasília (DF), Brazil

EXTRA-CURRICULAR COURSES

2012 The Biobased Economy: From Plant to Product (32h). Ghent University, Gent, Belgium.

2010 Assessing and communicating loss of biodiversity and ecosystem services (40h). Universität Bayreuth, Thurnau, Germany

2008 Economic valoration of environmental damages (*Valoração econômica de danos ambientais*) (12h). Associação Brasileira de Engenharia Sanitaria e Ambiental, Brasília (DF), Brazil.

2006 Industrial solid waste management (G*erenciamento de resíduos sólidos industriais*) (24h). Associação Brasileira de Engenharia Sanitaria e Ambiental, Joinville (SC), Brazil.

2005 Appropriate solutions for wastewater treatment of small communities (*Soluções Apropppriadas para Tratamento de Esgoto para Pequenas Comunidades*) (32h). Associação Brasileira de Engenharia Sanitaria e Ambiental. Florianópolis (SC), Brazil

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PROFESSIONAL/WORK EXPERIENCE

1. **Ghent University (Belgium)**
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   2010 - Current Researcher/PhD student (40h)

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   Place: Florianópolis (SC), Brazil
   2010 - 2010 Researcher (40h)
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   2003 - 2006 Junior researcher (20h)

3. **Companhia de Saneamento Ambiental do Distrito Federal – CAESB (Brazil)**
   Place: Brasília (DF), Brazil
   2007 - 2008 Environmental and Sanitation Engineer (40h)

4. **Empresa Júnior de Engenharia Sanitária e Ambiental – EJESAM (Brazil)**
   Place: Florianópolis (SC), Brazil
   2006 - 2006 President (15h)
   2005 - 2005 Project director (10h)
   2004 - 2004 Project assistant (5h)

5. **Rotária do Brasil Ltda. (Brazil)**
   Place: Florianópolis (SC), Brazil
   2006 - 2006 Trainee in Environmental and Sanitation Engineering (20h)

6. **Federação de Empresas Juniores de Santa Catarina - FEJESC (Brazil)**
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TEACHING EXPERIENCE

1. **Ghent University (Belgium)**
   Assistance to Prof. dr. ir. Jo Dewulf
   2010 Course: Clean Technology (12h) (Master in Bioscience Engineering)
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3. **Universidade Federal de Santa Catarina – UFSC (Brazil)**
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LANGUAGES SPOKEN

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REVIEWER OF SCIENTIFIC JOURNALS

- Journal of Cleaner Production (since 2011)
- Journal of Hazardous Materials (Print) (since 2012)
- Environmental Engineering and Management Journal (Print) (since 2012)

SCIENTIFIC PRODUCTION

1. **Papers published in international scientific journals**

- Alvarenga, R.A.F., Dewulf, J., Van Langenhove, H., Huijbregts, M.A.J., 2013. Exergy-based accounting for land as a natural resource in life cycle assessment. *The International Journal of Life Cycle Assessment*, v.18, pp. 939 - 947.
- Alvarenga, R.A.F., Dewulf, J., Van Langenhove, H., 2013. A new natural resource balance indicator for terrestrial biomass production systems. *Ecological Indicators*, v.32, pp. 140 - 146.
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- Alvarenga, R.A.F., Dewulf, J., De Meester, S., Wathelet, A., Villers, J., Thommeret, R., Hruska, Z., 2013. Life cycle assessment of bioethanol-based PVC. Part 2: Consequential approach. *Biofuels, Bioproducts and Biorefining*, DOI: 10.1002/bbb.1398.
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- Soares, S. R., Finotti, A. R., Silva Júnior, V. P., Alvarenga, R.A.F., 2012. Applications of life cycle assessment and cost analysis in Health Care Waste management. *Waste Management (Elmsford)*, v.33, pp. 175 - 183.
- Alvarenga, R.A.F., Silva Júnior, V.P., Soares, S.R., 2012. Comparison of the ecological footprint and a life cycle impact assessment method for a case study on Brazilian broiler feed production. *Journal of Cleaner Production*, v.28, pp. 25 - 32.
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2. Books or book chapters

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3. Publications in conferences proceedings

- Alvarenga, R.A.F., Dewulf, J., Van Langenhove, H. 2011. Accounting land as natural resource for energetic and exergetic LCA: A new method. *Workshop on Quantifying and Managing Land Use Effects of Bioenergy*, Campinas, Brazil.
- Zanghelini, G.M., Alvarenga, R.A.F., Soares, S. R. 2011. Life cycle assessment of an air reservoir, component of an air compressor. *Life Cycle Management - LCM 2011*, Berlin, Germany.
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4. Presentations in conferences

- Alvarenga, R.A.F., Dewulf, J., De Meester, S., Wathelet, A., Villers, J., Thommeret, R., Hruska, Z. 2012. Attributional and Consequential Life Cycle Assessment of Bioethanol-based PVC. *SETAC Europe 18th LCA Case study symposium*. Copenhagen, Denmark (oral presentation)
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- Alvarenga, R.A.F., Silva Júnior, V.P., Soares, S. R. 2010. Carbon footprint of four different Brazilian chicken feed scenarios. *7th International Conference on Life Cycle Assessment in the Agri-Food sector*. Bari, Italy (poster).
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THESIS SUPERVISIONS

- Guilherme Marcelo Zanghelini. Avaliação do ciclo de vida de um reservatório para compressor a ar. Bachelor thesis - Environmental and Sanitation Engineering - Universidade Federal de Santa Catarina, 2010 (finished)
- Laurien Spruyt. Environmental sustainability assessment of an integrated forest biorefinery. Master thesis - Bioscience Engineering, Ghent University, 2013 (ongoing).
- Tom Vandermeersch. Environmental sustainability assessment of food waste valorization options. Master thesis - Bioscience Engineering, Ghent University, 2013 (ongoing).

10. APPENDIX

10.1 SUPPLEMENTARY MATERIAL FROM THE MANUSCRIPT OF CHAPTER 2

10.1.1 Forest systems (S1)

Detailed information of the two systems presented in Figure 2.1, exclusively for forests. Natural forest systems are sub-divided in four (Table 10.1).

Table 10.1: Description of forest types for the two systems from Figure 2.1 of the research paper.

Forest systems	**Natural system**				**Human-made system**
	Sustainable extraction	*Unsustainable extraction*	*(A) Natural managed forests*	*(B) Secondary managed forests*	
Classification according to Carle and Holmgren (2008)	"Primary"	"Primary"	"Modified natural"	"Modified natural" and "Semi-natural, planted"	"Semi-natural, assisted natural regeneration", "Plantation, productive", and "Plantation, protective"
Explanation	Natural Forests, where the human intervention is negligible. Extractions of forest products (fruits, natural gum) may happen, but in a small scale	Natural Forests with high human intervention, but only for extraction. The forest products are extracted much faster than their regrowth, leading to species' extinctions, or deforestation	Natural Forests, where the human intervention is moderate, and the extractions may occur at a high rate, but in a sustainable way	Secondary forests (may be planted) with low human intervention during its growth, allowing it to work similar to a natural forest. The forestry processes are extensive	Forest with high human interference during the whole forest cycle (intensive management)
Net Primary Production	= Potential NPP	= Potential NPP	≈ Potential NPP	≈ Potential NPP	≠ Potential NPP (usually)
Biotic extraction (harvesting)	Negligible or few (sustainable)	Unsustainable	Sustainable	Ssustainable	Similar to agriculture harvest
Forestry	Negligible (small scale)	Intensive	Extensive	Extensive	Intensive
The biomass extracted…	regenerates naturally	doesn't grow back (in a short time length)	regenerates naturally	is planted again or regenerates naturally	is planted again or regenerates naturally, but through intensive management

10.1.2 Exergy calculations (S2)

For exergy calculations on biomass, we used two methods: (a) Group contribution; (b) By β-LHV. For both of them, the data was collected basically from Phillys Database (Phyllis, 2011) (except for '*roots from grass'*, where we got from Saunders et al. (2006), since Phillys database didn't have it). Depending on the data available, we performed the calculations for either method. For the data in which information was available on the chemical compounds and their percentage, we performed the group contribution method, and for the data where there was available only information on the atomic percentage of carbon, oxygen, nitrogen, and hydrogen, and their LHV, we performed the calculations of the method (b).

For method (a), we needed the exergy for several chemical compounds: (1) Cellulose; (2) Hemicellulose; (3) Starch; (4) Lignin; (5) Total non-structural carbohydrates; (6) Proteins; (7) Lipids; (8) Oils; (9) Extractives, hot water; (10) Ash; among others that we did not consider (e.g., extractives EtOH/toluene). The procedure to obtain the exergy value of each chemical compound will be explained below:

10.1.2.1 Cellulose

For cellulose we considered the polymer of glucose (Figure 10.1). The molecular weight considered was 162.1402 g/mol and the chemical exergy was 3005.89 kJ/mol. Therefore, the exergy value is 18.54 MJex/kgDM.

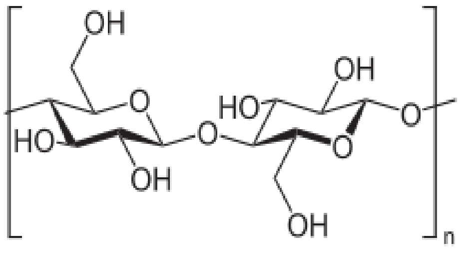

Figure 10.1: Polymer of cellulose

10.1.2.2 Hemicellulose

For Hemicellulose we considered the polymer of Xylan (Figure 10.2), as it is considered as the most abundant in hemicellulose. The molecular weight considered was 951.804 g/mol and the chemical exergy was 18986.59 kJ/mol. Therefore, the exergy value is 19.95 MJex/kgDM.

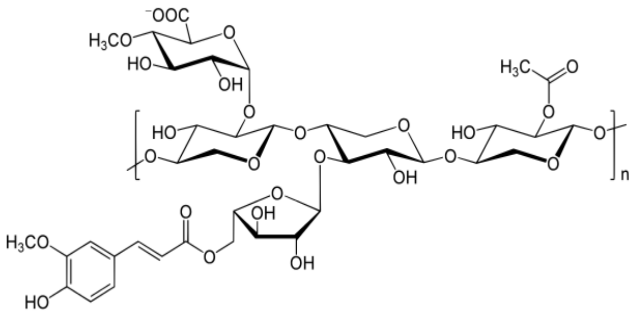

Figure 10.2: Polymer of Xylan

10.1.2.3 Starch

For starch we considered starch, per se (Figure 10.3). The molecular weight considered was 162.1402 g/mol and the chemical exergy was 3005.89 kJ/mol. Therefore, the exergy value is 18.54 MJex/kgDM.

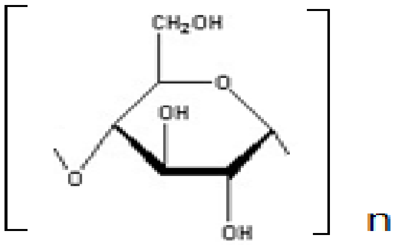

Figure 10.3: Polymer of Starch considered in the study

10.1.2.4 Lignin

For lignin, we considered a polymer that is most seen in the lignin structure (Figure 10.4). With a molecular weight of 179.1921 g/mol and a chemical exergy of 5220.45 kJ/mol, its exergy value is 29.13 MJex/kgDM.

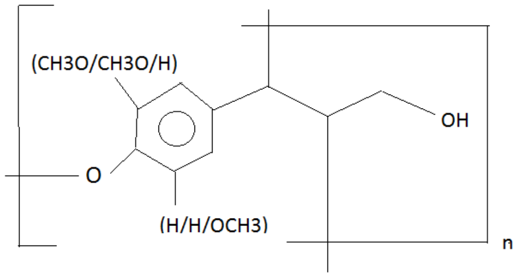

Figure 10.4: Polymer of Lignin considered in the study

10.1.2.5 Total non-structural carbohydrates

For Total non-strucutral carbohydrates, we considered an average value of glucose, fructose, and sucrose. Their exergy values were either calculate through group contribution method, or obtained in tables from Szargut et al. (1988), and were respectively: 16.52 MJex/kgDM, 16.38 MJex/kgDM, and 17.55 MJex/kgDM. Therefore, the average value used for the compound was 16.82 MJex/kgDM. The chemical structure of them are presented below (Figure 10.5).

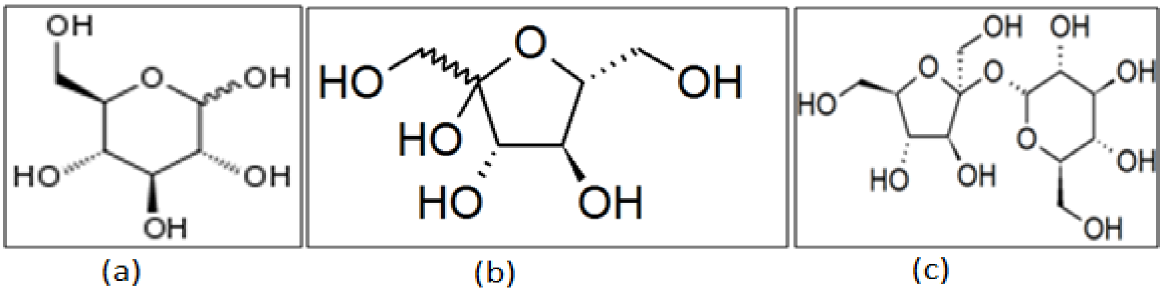

Figure 10.5: Chemical structure of glucose (a), fructose (b), and sucrose (c)

10.1.2.6 Proteins

For proteins, we searched in literature which would be the most abundant aminoacids in plants. We used data from three different authors: (a) Akubugwo et al. (2007) considered the aminoacids in *Amaranthus hybridus* leaves; (b) Glew et al. (2010) considered the aminoacids present in shoots and leaves from *Abrus precatorius*, the nuts from *Burnatia enneandra* and the leaves and stems from *Cadaba farinose*, and finally, (c) Yeoh et al. (1984) considered the amino acids present in Mimosoideae species, Caesalpinioideae species, and Papilionoideae species. We considered only the ten most abundant amino acids. We used the average results, coming up with the following numbers (Table 10.2):

Table 10.2: Average composition and exergy value of aminoacids considered for proteins in biomass

Aminoacid	Average composition	Exergy of their polymers (MJ_{ex}/kgDM)
Glutamic acid	22.6%	19.21
Aspartic acid	16.8%	15.89
Leucine	11.3%	32.90
Proline	7.7%	30.73
Arginine	7.2%	25.87
Serine	7.0%	18.63
Phenylalanine	7.0%	32.93
Lysine	7.0%	30.52
Alanine	6.8%	24.96
Glycine	6.6%	19.78
Average	100%	23.71

10.1.2.7 Lipids and Oils

For lipids and oils, we considered an average value of triglycerides. Through literature (Glew et al., 2010; Rezanka and Rezanková, 1999) we made an average composition of triglycerids monomers present in some plants: (a) Glew et al. (2010) considered the fatty acids present in shoots and leaves from *Abrus precatorius*, the nuts from *Burnatia enneandra* and the leaves and stems from *Cadaba farinose*; while Rezanka and Rezanková (1999) considered the fatty acids present in vegetable oils (from corn, cotton, grape, olive, peanut, soy, palm, cocoa, and sunflower). We considered only the five most abundant fatty acids. The average contribution of each monomer and their exergy value, presented below (Table 10.3):

Table 10.3: Average composition and exergy value of triglycerids' monomers considered for the average composition for triglycerides in biomass

Monomer of the triglycerides		Average composition	Exergy of their triglycerides (MJ_{ex}/kgDM)
Linoleic acid	(C18:2)	34.83%	39.46
Oleic acid	(C18:1)	26.57%	39.74
Palmitic acid	(C16:0)	21.83%	39.35
Stearic acid	(C18:0)	10.03%	40.02
Linolenic acid	(C18:3)	6.74%	39.17
Average		100%	39.55

10.1.2.8 Extractives, hot water

As was done for proteins and for lipids and oils, for Extractives (hot water), we searched in literature what would be the most abundant extractives from hot water in biomass. We used the substances and their amount presented by Hartonen et al. (2007) considering only the four most abundant ones. Their average amount and exergy values are presented below (Table 10.4):

Table 10.4: Average composition and exergy value of extractives, from hot water, considered for the compound 'Extractives, hot water'

Extractives	Amount of each extractive in biomass	Exergy of each extractive (MJ_{ex}/kgDM)
Dihydrokaempferol (aromadendrin)	44%	24.14
Naringin	27%	22.88
Naringenin	25%	26.30
Taxifolin	3%	22.35
Average	100%	24.29

10.1.2.9 Ash

For Ash in biomass, we used the mixture considered in Brehmer et al. (2008) which consists of: 35% of SiO2, 30% of K2O, 15% of CaO, 10% of P2O5, 5% of MgO and 5% of Na2O. We simply made a weighted sum of their exergy values, obtaining a final value of **2.11 MJex/kgDM**

10.1.2.10 Exergy values for the group composition method

Table 10.5: Exergy values considered

Compound	Exergy value (MJ_{ex}/kgDM)
Cellulose	18.54
Hemicellulose	19.95
Starch	18.54
Lignin	29.13
Total non-structural carbohydrates	16.82
Proteins	23.71
Lipids	39.55
Oils	39.55
Extractives, hot water	24.29
Ash	2.11

10.1.2.11 Calculation of the conversion factor, from carbon to exergy

In this section we will present the calculation of the conversion factor of the Oak tree, for illustration:

Oak tree: For this species, there was data available only on the wood and leaves, at Phyllis database. Data on roots were not available and therefore we used data from "Wood, pine roots” (the only available data on roots from trees in this database). The data used for the oak tree, for the three compartments (roots, wood, leaves) are in Table 10.6.

Table 10.6: Data used for Oak tree

Compartment	Roots	Leaves	Wood
Name at Phyllis database	*Wood, pine roots*	*Fallen leaves, oak*	*Wood, oak*
HHVdry (kJ/kgDM)			19078
LHVdry (kJ/kgDM)			17769
C (% of DM)			49.5
H (% of DM)			6.0
O (% of DM)			44.5
N (% of DM)			0.0
Cellulose (g)	44.6	29.6	
Hemicellulose (g)	25.6	26.4	
Lignin (g)	31.3	24	
Lipids (g)	0	10.1	
Protein (g)	0	4.4	
Extractives hot water (g)	0	11	
Total (g)	101.5	105.5	

The roots and leaves were calculated with the group contribution method, using the data from Table 10.5 and Table 10.6. The wood was calculated through the β-LHV, using equation 10.1 and 10.2.

$$\text{Chemical exergy} = \beta \text{ x LHV} \tag{10.1}$$

$$\beta = \frac{1.044+0.016\cdot H/_C-0.3493\cdot O/_C\times(1+0.053\cdot H/_C)+0.0493\cdot N/_C}{1-0.4124\cdot O/_C} \tag{10.2}$$

The values to be put in equation 10.2 are supposed to be the atomic ratio of the elements. Therefore, in the case of the data from Oak wood, the values to be put in equation 10.2 are presented in Table 10.7 (atomic ratio).

Table 10.7: Transformation of the atomic fraction to the atomic ratio

Elements	Percentage (%)	Atomic weight	Atomic ratio
C	49.5	12	4.12
H	6.0	1	6.00
O	44.5	16	2.78
N	0.0	14	0.00

The values from the column "atomic ratio", from Table 10.7, were implemented to equation 10.2, and can be seen in equation 10.3. From the result of β (1.127), we calculated the chemical exergy value of Oak wood (equation 10.4). After this we multiplied the chemical exergy value of each compartment (e.g. leaves) with the respective percentage of NPP from the biome "Temperate broadleaf and mixed forest", from Luyssaert et al. (2007), obtaining a chemical exergy value per mass of dry matter, as demonstrated in Table 10.8.

$$\beta = \frac{1.044+0.016\times(6.00/4.12)-0.3493\times(2.78/4.12)\times[1+0.053\times(6.00/4.12)]+0.0493\times(0/4.12)}{1-0.4124\times(2.78/4.12)} = 1.127 \quad (10.3)$$

$$\text{Chemical exergy} = \beta \text{ x LHV} = 1.127 \text{ x } 17769 = 20025 \text{ kJ}_{ex}/\text{kgDM} = 20.025 \text{ MJ}_{ex}/\text{kgDM} \quad (10.4)$$

Table 10.8: Chemical exergy value of Oak tree from a "Temperate broadleaf and mixed forest" biome

	Roots	Leaves	Wood
Chemical exergy value (MJ_{ex}/kgDM)	22.1	24.1	20.0
Fraction contributing to the total NPP at the respective biome (Luyssaert et al., 2007)	37%	23%	39%
Chemical exergy value of the NPP from Oak tree, from a Temperate broadleaf and mixed forest biome (MJ_{ex}/kgDM)		21.5	

Considering that 1 kgDM contains 0.5 kg of carbon (a common conversion factor used in literature), we obtained a chemical exergy of 43.0 MJ_{ex}/kgC for the Oak tree from Temperate broadleaf and mixed forest biome. The same procedure was done for all other species with data available in Phyllis database, for the same biome, and an average value for the aforementioned biome was calculated. This was done in all biomes (except mangroves), and an average conversion factor was obtained, as expressed in Table 10.9.

Table 10.9: Conversion factors for thirteen biomes and their average value (which was used in the manuscript)

Biome – according to Olson et al. (2001)	Conversion factor (MJ_{ex}/kgC)
Tropical and subtropical moist broadleaf forests	43.4
Tropical and subtropical dry broadleaf forest	43.0
Tropical and subtropical coniferous forests	43.9
Temperate broadleaf and mixed forests	43.2
Temperate coniferous forests	43.7
Boreal forests/taiga	43.0
Mediterranean forests, woodlands, and scrub or Sclerophyll forests	42.7
Tropical and subtropical grasslandas, savannas, and shrublands	41.7
Temperate grasslandas, savannas, and shrublands	43.0
Flooded grasslands and savannas	42.1
Montane grasslands and shrublands	42.6
Tundra	41.2
Desert and xeric shrublands	43.5
Average value (used in the manuscript)	**42.9**

10.1.3 Information on the products from case study 1 (S3)

In the Table 10.10, it can be seen the LCI inventory considered in the case study, for $1m^3$ of round wood, in a forest road. For the first case (human-made), we based the data on a process from ecoinvent database (Ecoinvent, 2010) called "*Roundwood, paraná pine (SFM), under bark, u=50%, at forest road/BR*". According to ecoinvent report, this type of wood is produced both in plantations and managed natural forests, but for our case study we assumed it was produced exclusively in plantations, therefore human-made systems. For the second case, which is also from a human-made system, we considered the data from the ecoinvent process called "*Roundwood, eucalyptus ssp. (SFM), under bark, u=50%, at forest road/TH*". For natural system, we used data from the process "*Roundwood, meranti (SFM), under bark, u=70%, at forest road/MY*", and from the process "*Round wood, azobe (SFM), under bark, u=30%, at forest road"*. A discussion on the quality of the data from ecoinvent database for round wood, used in the case studies, is out of the scope of this paper.

Table 10.10: Land resources inventoried in the life cycle of the four products used in case study 1 (according to ecoinvent database), with function unit of $1m^3$

System	Process name	Land resources inputs	
		Energy (in biomass, HHV) (MJ)	Land occupation (m^2.year)
Human-made	Parana Pine (Brazil)	13,032.00	6,120.00
Human-made	Eucalyptus (Thailand)	24,294.00	360.00
Natural	Meranti (Malaysia)	19,068.00	32,600.00
Natural	Azobe (Cameroon)	26,513.00	17,940.00

10.1.4 Information on the products from case study 2 (S4)

The name of the processes used in case study 2 can be seen in Table 10.11. Except for Barley from France and Wheat grains from Spain, the other seven processes did not have details on the region where the data came from. For this reason, we assumed specific regions for them, which are also in the table below.

Table 10.11: Information regarding case study 2, on the processes' names at ecoinvent database (Ecoinvent, 2010)

Process' name	Country (region)
Barley grains conventional, Barrois, at farm/FR	France (Barrois)
Wheat grains conventional, Castilla-y-Leon, at farm/ES	Spain (Castilla-y-Leon)
Corn, at farm/US	USA (Illinois)
Potatoes, at farm/US	USA (Washington)
Soybeans, at farm/BR	Brazil (Mato Grosso)
Sugarcane, at farm/BR	Brazil (Sao Paulo)
Sweet sorghum grains, at farm/CN	China (Jiangsu)
Palm fruit bunches, at farm/MY	Malaysia (Sarawak)
Roundwood, eucalyptus ssp. (SFM), under bark, u=50%, at forest road/TH	Thailand (Khon Kaen)

10.1.5 Maps with larger scale (S5)

In order to better visualize, through maps, the variability of data with a continent or a country, we elaborated several figures of maps, with larger scales. The legend used in the map from Figure 2.2, from the manuscript, was kept the same for all the other figures, for better visualization.

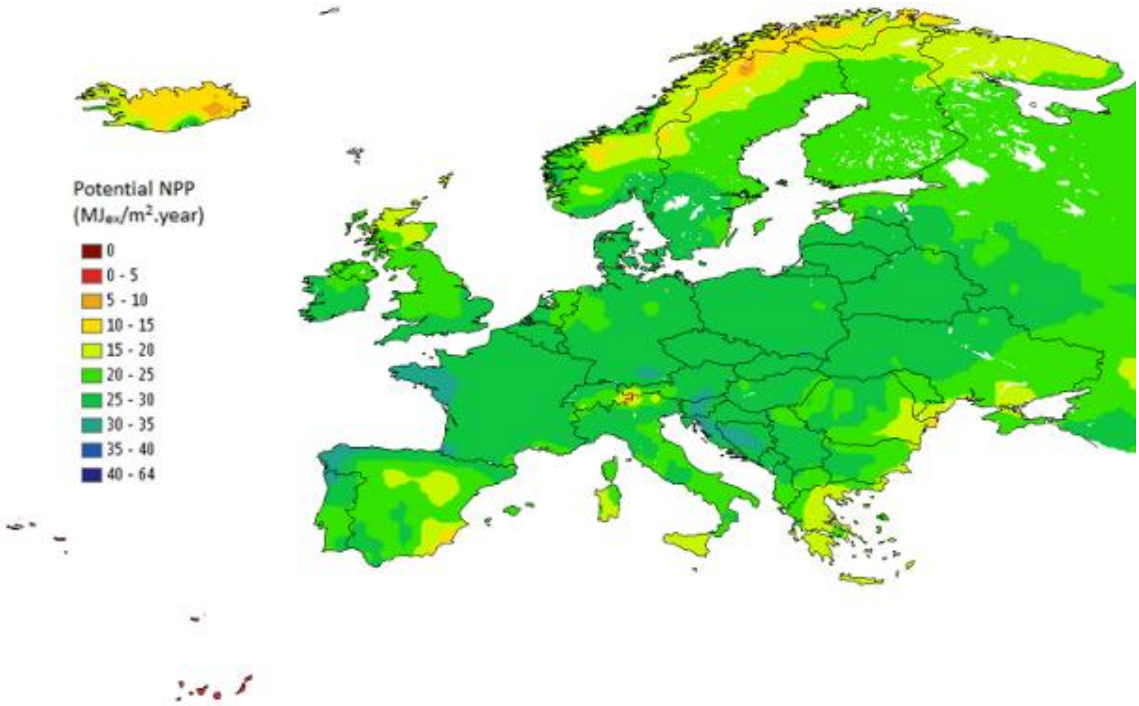

Figure 10.6: Characterization factors (for human-made systems) in Europe

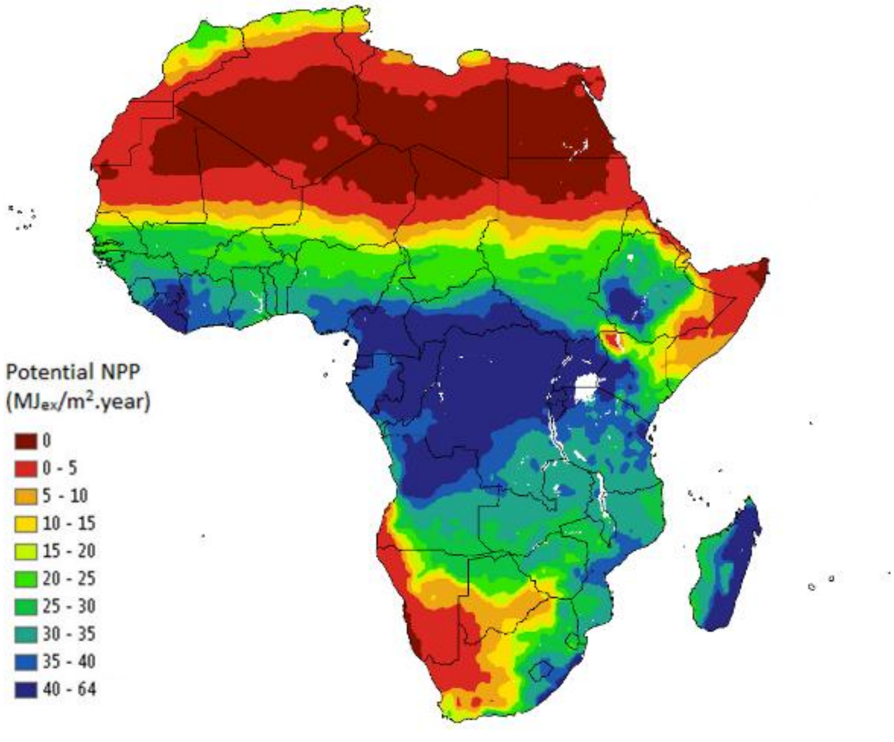

Figure 10.7: Characterization factors (for human-made systems) in Africa

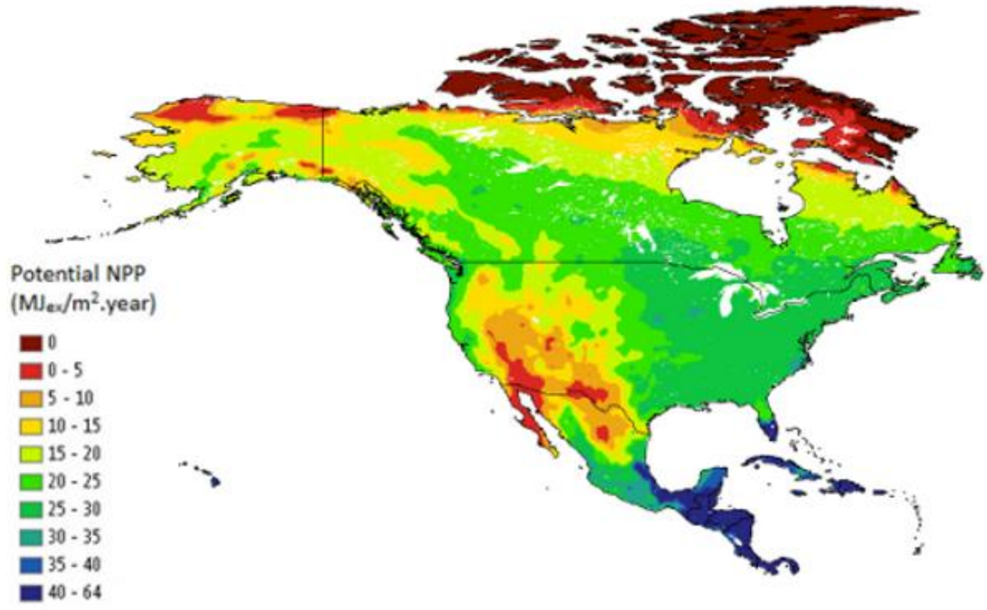

Figure 10.8: Characterization factors (for human-made systems) in North America, Central America, and Caribbean

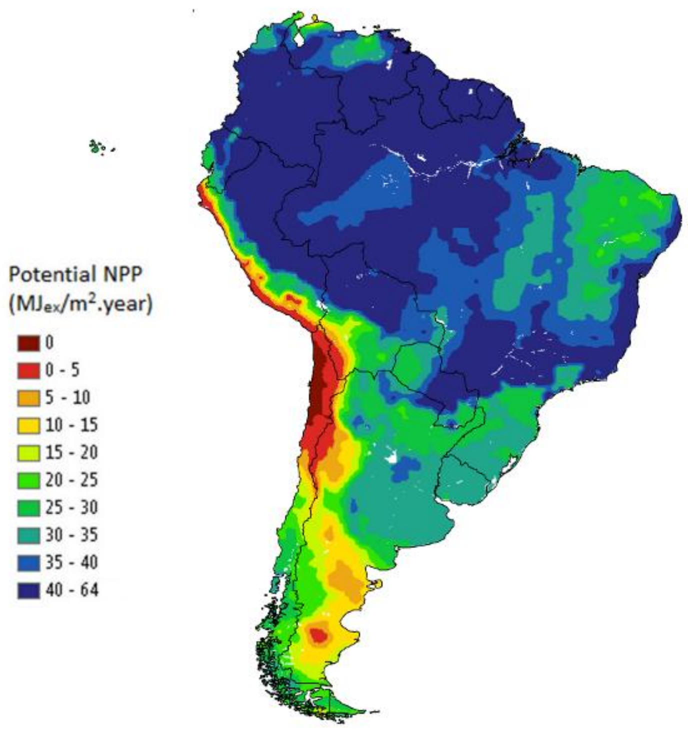

Figure 10.9: Characterization factors (for human-made systems) in South America

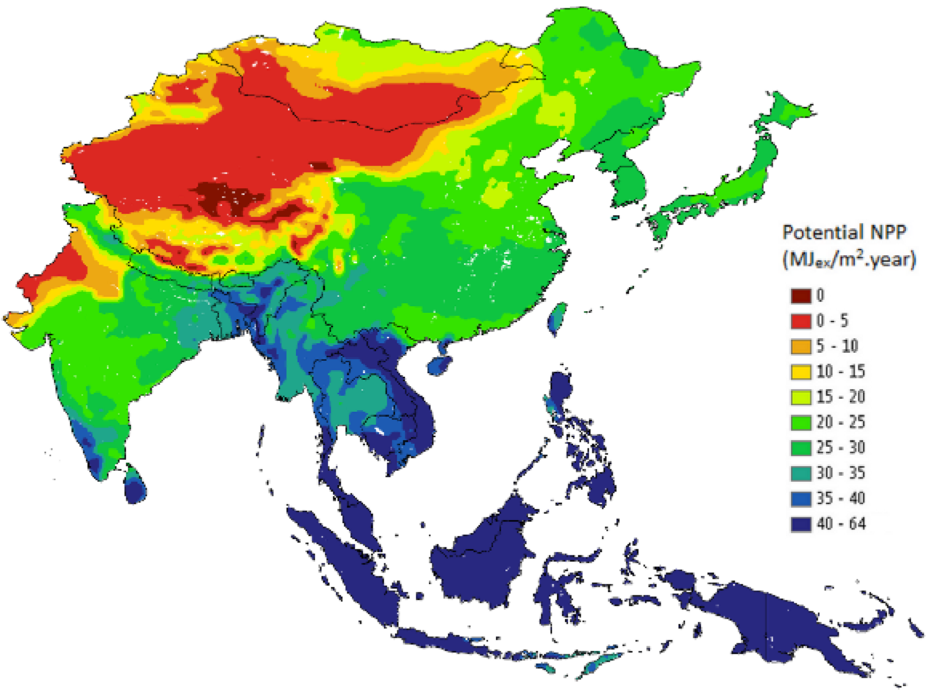

Figure 10.10: Characterization factors (for human-made systems) in Asia (east)

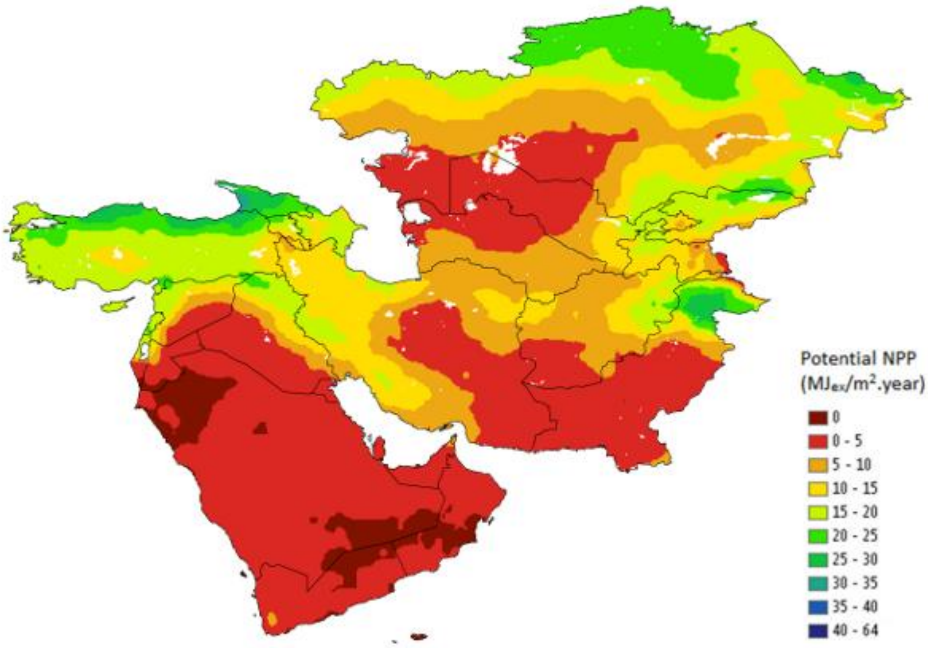

Figure 10.11: Characterization factors (for human-made systems) in Asia (west)

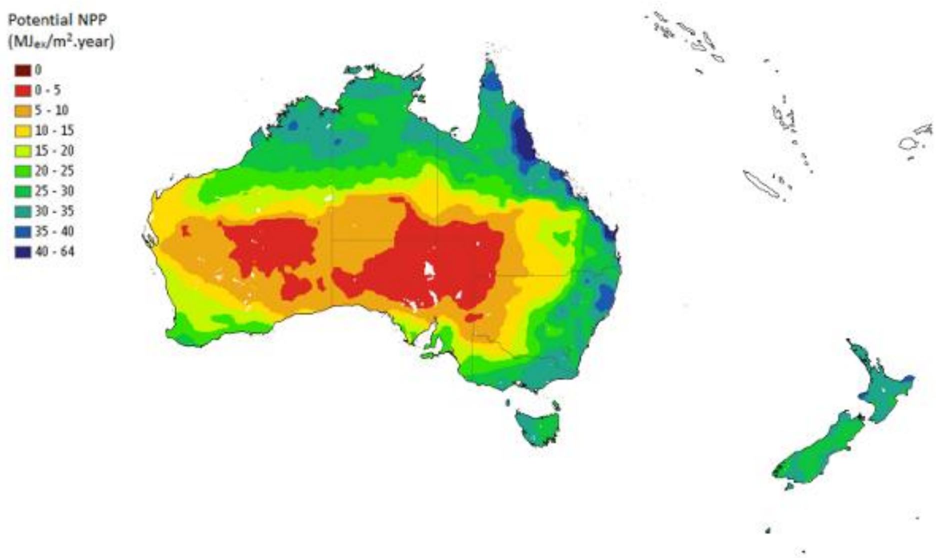

Figure 10.12: Characterization factors (for human-made systems) in Oceania and Australia (which is sub-divided in administrative regions)

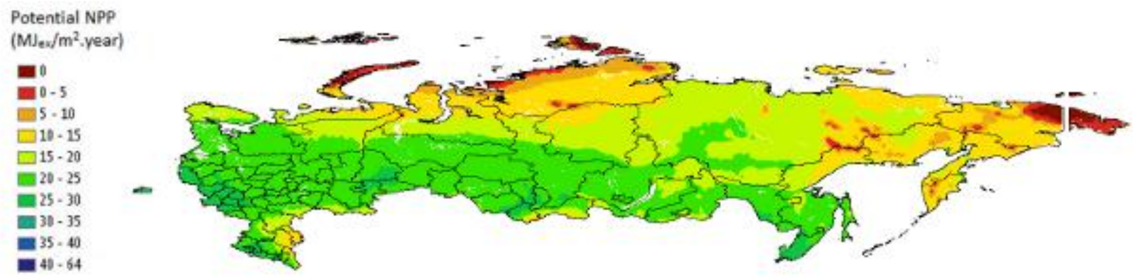

Figure 10.13: Characterization factors (for human-made systems) in Russia

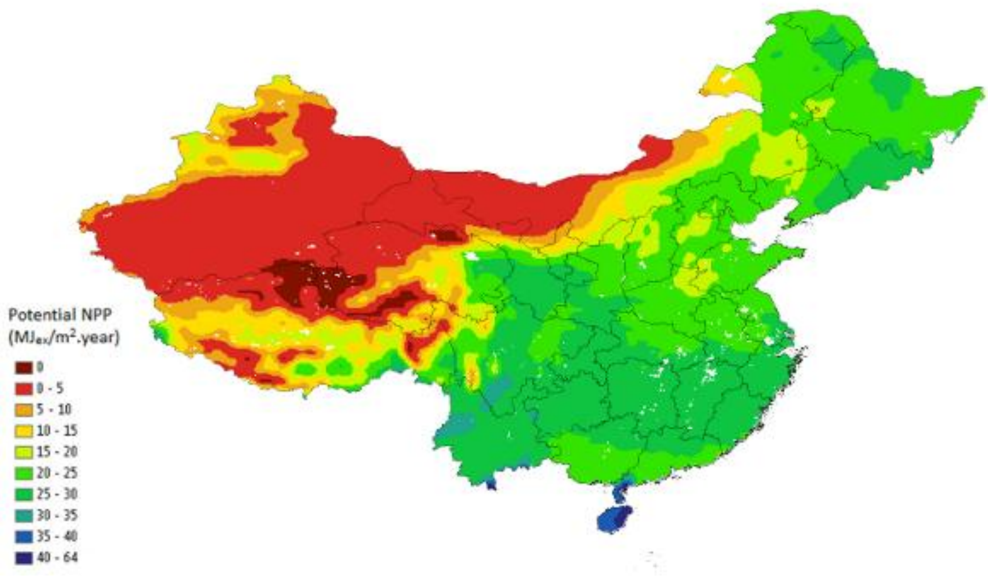

Figure 10.14: Characterization factors (for human-made systems) in China

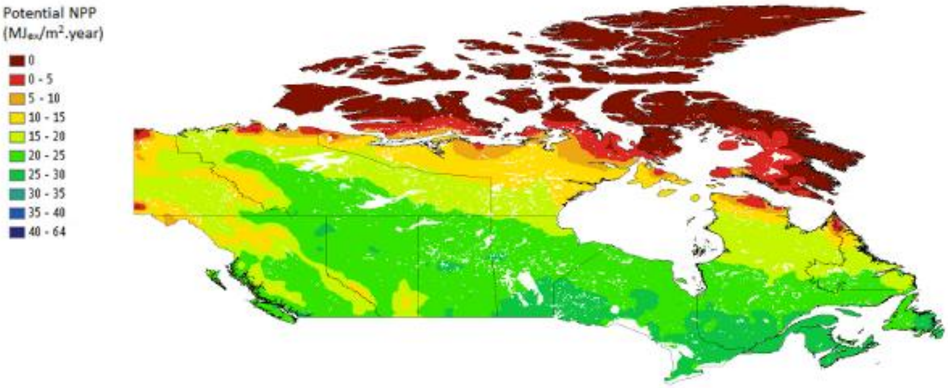

Figure 10.15: Characterization factors (for human-made systems) in Canada

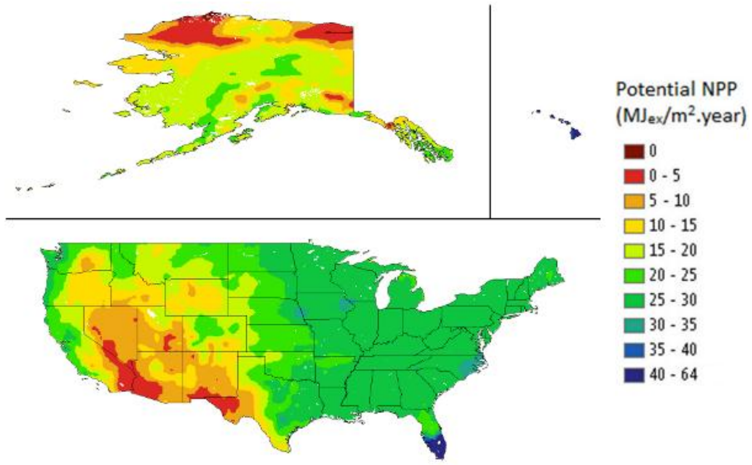

Figure 10.16: Characterization factors (for human-made systems) in the USA

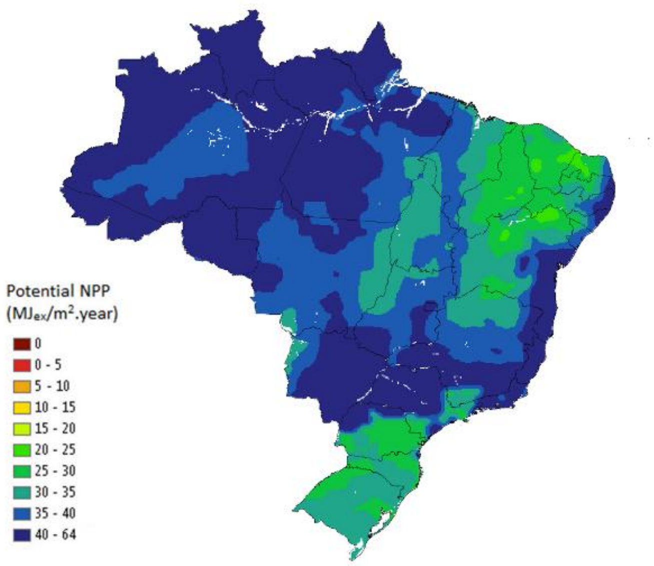

Figure 10.17: Characterization factors (for human-made systems) in Brazil

10.1.6 Files for the map with site-dependent CF (at grid level) (S6)

The image files and the ASCII file for the map with site-dependent CF can be accessed through the files available as supplementary material.

10.1.7 Site-dependent CF at country and regional level (S7)

We calculated the site-dependent CF of 165 countries (Table 10.12). We were not able to calculate site-dependent CF for other countries because the data was not available in Haberl et al. (2007). Note that the variability of the values for each country are related to the individual grid cells within each country, while the site-dependent CF are related to the weighted-to-the-area average from that country.

Table 10.12: Site-dependent CF at country level for 165 countries, with their variability in the values

		CF (MJ_{ex}/m^2.year)	Variability of the values (MJ_{ex}/m^2.year)	
Continent	Country	Mean value	2,5th percentile	97,5th percentile
Africa	Algeria	**1.8**	0.0	18.3
Africa	Angola	**33.1**	3.6	46.0
Africa	Benin	**27.8**	23.7	30.4
Africa	Botswana	**14.8**	3.0	28.1
Africa	Burkina Faso	**24.5**	18.6	29.2
Africa	Burundi	**43.9**	41.4	46.3
Africa	Cameroon	**39.3**	23.8	48.5
Africa	Central African Rep.	**39.0**	24.0	49.1
Africa	Chad	**10.5**	0.0	26.5
Africa	Congo	**45.3**	37.2	49.5
Africa	Côte d'Ivoire	**35.7**	29.4	42.5
Africa	Dem. Rep. of Congo	**42.6**	31.6	52.1
Africa	Djibouti	**11.5**	4.5	17.7
Africa	Egypt	**0.2**	0.0	2.1
Africa	Equatorial Guinea	**42.5**	39.8	45.4
Africa	Eritrea	**8.4**	1.0	20.8
Africa	Ethiopia	**25.7**	3.6	45.3
Africa	Gabon	**39.8**	36.7	47.0
Africa	Gambia	**24.7**	22.1	27.3
Africa	Ghana	**30.5**	25.9	35.5
Africa	Guinea	**32.3**	26.3	43.0
Africa	Guinea-Bissau	**26.1**	24.8	27.5
Africa	Kenya	**27.9**	5.3	59.6
Africa	Lesotho	**34.7**	29.4	38.5
Africa	Liberia	**41.5**	37.9	43.8
Africa	Libyan Arab Jamah.	**0.7**	0.0	7.1

Africa	Madagascar	**42.1**	27.0	59.3
Africa	Malawi	**31.8**	27.1	36.4
Africa	Mali	**11.0**	0.0	28.5
Africa	Mauritania	**2.8**	0.0	15.9
Africa	Morocco	**10.8**	0.5	23.8
Africa	Mozambique	**31.6**	26.1	38.1
Africa	Namibia	**8.6**	0.0	27.3
Africa	Niger	**6.2**	0.0	24.6
Africa	Nigeria	**28.3**	17.0	39.3
Africa	Rwanda	**46.3**	42.6	48.3
Africa	Senegal	**22.6**	10.6	28.3
Africa	Sierra Leone	**32.5**	29.8	36.8
Africa	Somalia	**5.4**	0.0	22.6
Africa	South Africa	**16.7**	1.7	39.3
Africa	Sudan	**14.9**	0.0	38.7
Africa	Swaziland	**27.0**	23.9	30.1
Africa	Togo	**29.5**	26.3	31.8
Africa	Tunisia	**6.3**	0.2	18.3
Africa	Uganda	**49.6**	33.3	59.0
Africa	United Rep. Tanzania	**35.5**	30.2	45.7
Africa	Western Sahara	**0.4**	0.0	0.9
Africa	Zambia	**31.2**	28.1	35.7
Africa	Zimbabwe	**27.0**	12.8	35.4
Asia	Afghanistan	**8.4**	0.3	18.8
Asia	Armenia	**16.0**	9.9	22.3
Asia	Azerbaijan	**15.8**	10.2	20.7
Asia	Bangladesh	**36.7**	30.8	43.1
Asia	Bhutan	**27.4**	12.8	33.6
Asia	Brunei Darussalam	**48.0**	46.2	50.2
Asia	Cambodia	**40.4**	34.5	46.5
Asia	China	**16.0**	0.0	29.0
Asia	Cyprus	**17.9**	16.6	20.0
Asia	Georgia	**25.9**	19.2	31.2
Asia	India	**23.5**	3.0	39.1
Asia	Indonesia	**49.2**	35.7	58.6
Asia	Iran (Islamic Rep. of)	**7.8**	0.4	15.7
Asia	Iraq	**6.7**	0.3	19.9
Asia	Israel	**7.5**	0.0	19.1
Asia	Japan	**25.7**	23.8	28.5
Asia	Jordan	**2.0**	0.0	12.8
Asia	Kazakhstan	**13.0**	2.9	22.9
Asia	Korea (Dem. Ppl's. Rep. of)	**26.0**	24.1	27.7
Asia	Korea (Republic of)	**27.2**	25.7	29.0
Asia	Kuwait	**2.2**	1.4	3.6
Asia	Kyrgyzstan	**16.2**	7.8	23.9
Asia	Lao People's Dem. Rep.	**42.0**	34.8	51.9
Asia	Lebanon	**18.3**	15.0	20.2

Asia	Malaysia	**48.3**	42.7	55.4
Asia	Myanmar	**34.0**	25.5	42.5
Asia	Nepal	**23.0**	3.0	31.2
Asia	Oman	**0.6**	0.0	2.4
Asia	Pakistan	**5.5**	0.0	27.2
Asia	Papua New Guinea	**48.5**	43.3	57.6
Asia	Philippines	**45.1**	35.1	52.5
Asia	Qatar	**1.0**	0.7	1.4
Asia	Republic of Mongolia	**8.2**	0.3	20.1
Asia	Saudi Arabia	**0.4**	0.0	1.9
Asia	Sri Lanka	**40.1**	27.9	49.3
Asia	Syrian Arab Republic	**9.7**	0.9	20.3
Asia	Taiwan	**33.7**	26.5	44.7
Asia	Tajikistan	**12.0**	3.7	16.5
Asia	Thailand	**36.3**	31.0	45.5
Asia	Turkey	**18.9**	13.0	28.1
Asia	Turkmenistan	**5.7**	2.5	9.9
Asia	United Arab Emirates	**0.9**	0.0	5.0
Asia	Uzbekistan	**6.8**	2.7	17.5
Asia	Viet Nam	**41.2**	22.5	52.2
Asia	Yemen	**0.9**	0.0	4.2
Asia/Europe	Russia Federation	**18.7**	3.0	25.3
Europe	Albania	**24.7**	22.5	27.9
Europe	Austria	**27.2**	17.8	30.3
Europe	Belarus	**26.2**	24.9	27.1
Europe	Belgium	**26.9**	25.3	27.7
Europe	Bosnia and Herzegovina	**29.7**	27.5	31.1
Europe	Bulgaria	**23.5**	19.4	27.0
Europe	Croatia	**28.7**	26.2	30.9
Europe	Czech Republic	**27.1**	25.8	28.2
Europe	Denmark	**26.4**	25.4	27.5
Europe	Estonia	**24.6**	22.6	25.6
Europe	Finland	**22.0**	15.7	23.8
Europe	France	**28.0**	24.0	30.6
Europe	Germany	**26.5**	24.7	29.9
Europe	Greece	**19.2**	16.9	22.9
Europe	Hungary	**26.2**	24.5	28.6
Europe	Iceland	**14.2**	9.0	22.9
Europe	Ireland	**25.7**	21.9	27.6
Europe	Island of Man	**24.7**	24.2	25.0
Europe	Italy	**23.8**	15.6	29.2
Europe	Latvia	**25.7**	24.9	26.6
Europe	Lithuania	**26.3**	25.5	26.9
Europe	Luxembourg	**27.2**	26.7	27.6
Europe	Macedonia (T.F. Yug. Rep.)	**22.9**	19.7	25.9
Europe	Moldova (Republic of)	**22.4**	18.7	25.0
Europe	Monaco	**26.7**	26.7	26.7

Europe	Montenegro	**28.6**	26.4	29.7
Europe	Netherlands	**25.3**	24.3	27.5
Europe	Norway	**19.5**	13.2	26.6
Europe	Poland	**27.4**	25.2	29.7
Europe	Portugal	**24.7**	4.2	31.4
Europe	Romania	**23.2**	16.0	27.0
Europe	Serbia	**26.5**	23.9	29.1
Europe	Slovakia	**28.2**	25.4	29.9
Europe	Slovenia	**29.8**	28.2	30.8
Europe	Spain	**23.0**	14.7	31.9
Europe	Sweden	**22.0**	12.3	27.5
Europe	Switzerland	**24.4**	12.0	28.8
Europe	Ukraine	**24.5**	18.5	28.8
Europe	United Kingdom	**23.2**	18.5	28.8
Central America	Belize	**49.8**	43.2	52.9
Central America	Costa Rica	**51.7**	38.3	62.7
Central America	El Salvador	**40.9**	37.8	43.8
Central America	Guatemala	**48.2**	40.3	55.7
Central America	Honduras	**50.9**	39.9	57.9
Central America	Nicaragua	**49.3**	36.3	58.5
Central America	Panama	**52.1**	45.6	63.6
Caribbean	Cuba	**39.7**	32.1	45.9
Caribbean	Dominican Republic	**51.3**	40.3	56.3
Caribbean	Haiti	**45.2**	34.2	54.9
Caribbean	Jamaica	**44.8**	43.5	46.8
Caribbean	Puerto Rico	**53.8**	51.2	55.0
Caribbean	Trinidad and Tobago	**44.9**	44.4	45.5
North America	Canada	**17.3**	0.0	26.2
North America	Mexico	**21.8**	1.5	46.0
North America	United States	**19.8**	3.0	29.3
Oceania	Australia	**17.3**	2.1	34.9
Oceania	New Zealand	**30.7**	26.2	35.1
South America	Argentina	**24.0**	4.8	36.6
South America	Bolivia	**34.6**	4.0	48.3
South America	Brazil	**38.8**	26.7	50.1
South America	Chile	**14.7**	0.0	30.6
South America	Colombia	**45.6**	31.5	56.0
South America	Ecuador	**39.2**	26.2	47.5
South America	French Guiana	**49.2**	47.0	51.5
South America	Guyana	**49.1**	46.2	53.9
South America	Paraguay	**36.8**	27.1	53.0
South America	Peru	**33.7**	1.2	51.0
South America	Suriname	**48.0**	46.2	50.5
South America	Uruguay	**31.7**	29.8	33.3
South America	Venezuela	**42.5**	25.5	55.2

We also calculated site-dependent CF at regional level for the six largest countries in area: (1) Russia, with 88 adminstrative regions; (2) Canada, with 13 adminstrative regions; (3) China, with 33 adminstrative regions; (4) USA, with 51 adminstrative regions; (5) Brazil, with 28 adminstrative regions; and (6) Australia, with 8 adminstrative regions. The values can be seen in Table 10.13. Note that the variability of the values for each region are related to the individual grid cells within each region, while the site-dependent CF are related to the weighted-to-the-area average from that region.

Table 10.13: Site-dependent CF at regional level for the six largest countries in area, with their variability in the values

		CF (MJ_{ex}/m^2.year)	Variability of the values (MJ_{ex}/m^2.year)	
Country	Administrative region	Mean value	2,5th percentile	97,5th percentile
Russia	Adygeya	27.7	25.6	29.8
Russia	Aga Buryat	20.0	18.0	21.0
Russia	Altay	23.1	19.8	26.2
Russia	Amur	22.2	17.2	25.6
Russia	Arkhangelsk	18.1	0.0	23.7
Russia	Astrakhan	12.4	8.7	15.9
Russia	Bashkortostan	23.5	21.4	25.1
Russia	Belgorod	23.4	21.8	25.2
Russia	Bryansk	26.0	24.9	27.0
Russia	Buryat	20.4	16.7	23.6
Russia	Chechnya	21.0	15.2	23.8
Russia	Chelyabinsk	24.3	22.2	25.9
Russia	Chita	20.5	17.1	22.8
Russia	Chukot	8.8	0.0	14.7
Russia	Chuvash	22.7	21.8	23.3
Russia	City of St. Petersburg	24.3	24.0	24.5
Russia	Dagestan	18.0	13.1	23.1
Russia	Evenk	17.0	10.5	22.0
Russia	Gorno-Altay	21.9	10.2	27.0
Russia	Ingush	24.5	23.2	25.5
Russia	Irkutsk	21.1	17.4	24.0
Russia	Ivanovo	23.0	22.1	23.4
Russia	Kabardin-Balkar	24.3	21.8	26.1
Russia	Kalingrad	27.0	26.8	27.2
Russia	Kalmyk	15.4	11.2	21.3
Russia	Kalunga	25.7	24.9	26.5
Russia	Kamchatka	12.5	5.0	18.7
Russia	Karachay-Cherkess	26.2	22.1	28.3
Russia	Karelia	22.7	20.6	23.9
Russia	Kemerovo	24.6	23.1	26.9
Russia	Khabarovsk	18.7	6.9	24.6

Russia	Khakass	24.4	22.4	26.2
Russia	Khanty-Mansiy	21.8	18.2	24.0
Russia	Kirov	23.5	22.4	24.2
Russia	Komi	19.4	13.6	23.0
Russia	Komi-Permyak	23.4	22.6	23.9
Russia	Koryak	13.6	7.1	17.2
Russia	Kostroma	23.1	22.0	24.1
Russia	Krasnodar	25.6	22.7	29.2
Russia	Krasnoyarsk	21.6	14.4	24.9
Russia	Kurgan	24.3	22.2	26.0
Russia	Kursk	25.8	24.8	26.6
Russia	Leningrad	24.2	23.5	24.9
Russia	Lipetsk	25.2	24.3	25.8
Russia	Maga Buryatdan	12.7	6.5	16.8
Russia	Mariy El	22.9	21.6	24.1
Russia	Mordovia	24.3	22.8	25.3
Russia	Moskva	24.1	22.7	25.5
Russia	Murmansk	18.2	16.0	21.4
Russia	Nenets	15.6	13.2	19.7
Russia	Nizhegorod	23.4	21.6	25.2
Russia	North Ossetia	25.7	23.3	26.4
Russia	Novgorod	24.5	23.4	25.1
Russia	Novoslbirsk	22.2	20.2	23.8
Russia	Omsk	22.2	20.0	24.0
Russia	Orel	26.4	25.7	26.9
Russia	Orenburg	20.3	17.0	23.2
Russia	Penza	24.0	23.0	25.2
Russia	Perm	23.4	20.7	24.4
Russia	Promorye	24.9	21.3	25.9
Russia	Pskov	25.3	24.7	25.8
Russia	Rostov	21.0	18.2	24.2
Russia	Ryazan	24.1	22.9	25.1
Russia	Sakha	17.0	9.4	20.5
Russia	Sakhalin	21.7	18.2	24.5
Russia	Samara	22.5	20.7	24.0
Russia	Saratov	20.7	16.9	23.1
Russia	Smolensk	25.5	24.4	26.2
Russia	Stavropol	22.1	16.5	27.1
Russia	Sverdlovsk	24.1	21.0	26.1
Russia	Tambov	24.4	22.7	25.3
Russia	Tatarstan	23.9	23.1	24.3
Russia	Taymyr	10.7	0.0	14.4
Russia	Tomsk	23.4	22.0	24.1
Russia	Tula	25.7	25.1	26.6
Russia	Tuva	19.5	11.7	24.2
Russia	Tver	24.5	22.7	25.2
Russia	Tyumen	23.5	22.6	25.0

Russia	Udmurt	23.6	22.7	24.5
Russia	Ulyanovsk	23.1	22.3	23.8
Russia	Ust-Orda-Buryat	21.4	20.4	22.7
Russia	Vladimir	23.4	22.5	24.0
Russia	Volgograd	19.0	16.2	21.7
Russia	Vologda	23.5	22.5	24.3
Russia	Voronezh	22.5	20.3	24.9
Russia	Yamal-Nenets	16.0	6.5	21.1
Russia	Yaroslavl	23.1	22.3	23.9
Russia	Yevrey	24.3	22.9	25.5
Canada	Alberta	22.5	14.7	24.9
Canada	British Columbia	19.9	12.8	24.9
Canada	Manitoba	23.6	18.8	27.5
Canada	New Brunswick	26.3	25.0	26.5
Canada	Newfoundland and Labrador	20.0	8.1	25.5
Canada	Northern Territories	15.2	0.0	23.7
Canada	Nova Scotia	26.1	25.1	27.7
Canada	Nunavut	5.0	0.0	16.4
Canada	Ontario	24.8	21.8	26.9
Canada	Prince Edward Island	24.8	24.1	26.2
Canada	Quebec	20.8	6.1	26.6
Canada	Saskatchewan	23.5	18.8	27.5
Canada	Yukon	15.3	3.6	20.6
China	Anhui	24.3	21.4	27.6
China	Beijing	20.6	18.8	22.5
China	Chongqing	26.6	24.7	28.0
China	Fujian	28.1	24.2	29.2
China	Gansu	12.9	0.1	27.6
China	Guangdong	26.4	21.5	39.0
China	Guangxi	24.4	21.2	27.6
China	Guizhou	28.1	25.5	29.7
China	Hainan	39.6	36.7	42.5
China	Hebei	21.5	18.7	24.7
China	Heilongjiang	23.8	19.9	26.0
China	Henan	21.9	18.0	25.0
China	Hong Kong	24.4	24.3	24.6
China	Hubei	24.9	22.1	27.5
China	Hunan	26.8	25.2	27.9
China	Jiangsu	24.4	21.2	27.3
China	Jiangxi	27.3	26.0	28.4
China	Jilin	24.1	19.9	26.7
China	Liaoning	23.1	19.5	27.3
China	Macau	24.3	24.3	24.3
China	Nei Mongol / Inner Mongolia	13.2	0.3	25.1
China	Ningxia Hui	17.0	4.3	27.1
China	Qinghai	7.7	0.0	26.0
China	Shaanxi	23.4	16.5	26.8

China	Shandong	22.0	17.8	24.6
China	Shanghai	27.7	26.8	28.0
China	Shanxi	21.1	18.1	23.6
China	Sichuan	24.0	8.8	30.9
China	Tianjin	20.9	20.3	22.3
China	Xinjiang Uygur	2.9	0.0	15.3
China	Xizang/Tibet	10.3	0.0	25.8
China	Yunnan	28.4	24.3	32.9
China	Zhejiang	27.3	24.9	28.8
USA	Alabama	27.4	25.8	29.4
USA	Alaska	14.7	0.8	21.0
USA	Arizona	7.4	0.9	15.0
USA	Arkansas	25.8	24.2	28.3
USA	California	15.3	1.1	25.3
USA	Colorado	17.0	8.7	22.5
USA	Connecticut	27.3	26.8	27.9
USA	Delaware	27.9	27.0	28.3
USA	District of Columbia	25.9	25.8	25.9
USA	Florida	31.6	23.5	52.2
USA	Georgia	27.1	25.2	29.5
USA	Hawaii	46.7	37.6	55.1
USA	Idaho	15.4	9.4	22.6
USA	Illinois	28.6	26.2	29.8
USA	Indiana	27.1	25.9	28.2
USA	Iowa	29.0	27.3	30.4
USA	Kansas	22.5	18.3	25.5
USA	Kentucky	26.6	25.4	28.2
USA	Louisiana	26.4	25.1	27.4
USA	Maine	25.7	24.9	27.0
USA	Maryland	27.2	25.3	28.8
USA	Massachussets	27.3	26.7	27.7
USA	Michigan	26.0	24.5	27.9
USA	Minnesota	27.5	25.6	29.3
USA	Mississippi	27.7	26.0	29.0
USA	Missouri	26.7	24.9	28.8
USA	Montana	19.4	14.1	24.3
USA	Nebraska	22.7	16.4	30.9
USA	Nevada	7.2	3.6	13.5
USA	New Hampshire	26.3	25.2	27.4
USA	New Jersey	27.2	26.4	27.9
USA	New Mexico	9.0	3.6	16.2
USA	New York	27.0	25.8	28.0
USA	North Carolina	29.0	26.1	31.2
USA	North Dakota	24.9	21.0	27.2
USA	Ohio	27.4	26.4	28.8
USA	Oklahoma	23.2	17.2	27.1
USA	Oregon	16.5	10.6	27.7

USA	Pennsylvania	27.9	27.0	28.8
USA	Rhode Island	27.2	27.0	27.4
USA	South Carolina	27.0	25.5	29.3
USA	South Dakota	22.4	18.3	27.3
USA	Tennessee	27.0	25.2	28.8
USA	Texas	19.2	3.8	28.3
USA	Utah	9.9	4.6	18.3
USA	Vermont	26.1	25.0	26.9
USA	Virginia	27.0	25.4	30.0
USA	Washington	19.3	8.4	28.2
USA	West Virginia	28.2	27.2	29.3
USA	Wisconsin	28.1	26.0	30.0
USA	Wyoming	14.5	9.8	20.0
Brazil	Acre	43.3	40.6	48.2
Brazil	Alagoas	36.7	27.3	45.9
Brazil	Amapa	43.9	39.5	49.5
Brazil	Amazonas	41.6	39.0	48.3
Brazil	Bahia	35.2	24.6	51.4
Brazil	Ceara	27.5	24.5	31.8
Brazil	Distrito Federal	40.5	39.3	40.9
Brazil	Espirito Santo	47.8	42.9	50.1
Brazil	Goias	38.1	33.2	44.1
Brazil	Maranhao	34.5	28.2	39.5
Brazil	Mato Grosso	38.5	33.1	42.6
Brazil	Mato Grosso do Sul	44.8	34.3	50.4
Brazil	Minas Gerais	38.4	30.0	47.0
Brazil	Para	40.9	35.0	46.1
Brazil	Paraiba	32.1	26.1	42.8
Brazil	Parana	34.8	28.5	52.7
Brazil	Pernambuco	33.0	25.2	46.2
Brazil	Piaui	28.7	25.1	34.8
Brazil	Rio de Janeiro	43.3	39.1	47.6
Brazil	Rio Grande do Norte	28.3	23.6	38.7
Brazil	Rio Grande do Sul	30.8	28.3	33.7
Brazil	Rondonia	42.6	40.3	45.0
Brazil	Roraima	47.6	41.7	52.9
Brazil	Santa Catarina	30.6	28.4	34.0
Brazil	Sao Paulo	42.2	29.3	50.6
Brazil	Sergipe	35.0	27.5	39.9
Brazil	Tocantins	34.7	32.9	37.7
Australia	Australian Cap. Terr. and Jervis Bay Terr.	29.3	28.1	30.3
Australia	New South Wales	20.2	3.9	35.6
Australia	Northern Territory	20.6	3.6	33.0
Australia	Queensland	21.6	2.5	43.0
Australia	South Australia	6.3	1.4	22.7
Australia	Tasmania	30.3	27.4	34.2
Australia	Victoria	25.2	8.1	33.8

Australia	Western Australia	14.6	3.4	32.9

10.1.8 CF of land resources implemented into ecoinvent reference flows (S8)

The ecoinvent database does not support fully the framework proposed by this paper, through the existing reference flows. Therefore, in this section we proposed more specific reference flows to this database, in order to support our framework, and applied the site-generic CF.

Because most of the data from ecoinvent is from Western Europe, the CF implemented for human-made systems was the site-dependent CF, at continent level, for Europe (23.20 MJ_{ex}/m^2.year). The land occupation reference flows which received a zero value were considered to be from natural systems. The site-generic CF are presented in Table 10.14.

The data from Haberl et al. (2007) is related only for the terrestrial potential NPP, and ecoinvent database also considers occupation of sea waters ("*Occupation, sea and ocean*"). Therefore, for that reference flow we needed to consider data from another source. We considered the average value for Western European sea waters (Mediterranean Sea and Northeastern Atlantic Sea) from Saba et al. (2011). Then, we multiplied this average value of NPP, in gC/m^2a, by a phytoplankton-exergy conversion factor that was calculated by the chemical composition of microalgae, available in Phyllis database (Phyllis, 2011) and through the β-LHV method (there was not enough data to proceed the exergy calculation through group contribution method). As a result, we obtained a CF of 10.04 MJ_{ex}/m^2a.

Table 10.14: Reference flows from ecoinvent adjusted to the framework proposed in this paper, with the site-generic CF for land resources

System	Reference flow	CF for land resources	Unit
Natural	Energy, gross calorific value, in biomass, natural system	1.06	MJ_{ex}/MJ
Human-made	Energy, gross calorific value, in biomass, human-made system	0.00	MJ_{ex}/MJ
Human-made	Occupation, arable	23.20	MJ_{ex}/m^2a
Human-made	Occupation, construction site	23.20	MJ_{ex}/m^2a
Human-made	Occupation, dump site	23.20	MJ_{ex}/m^2a
Human-made	Occupation, dump site, benthos	0.00	MJ_{ex}/m^2a
Natural	Occupation, forest, natural system	0.00	MJ_{ex}/m^2a
Human-made	Occupation, forest, human-made system	23.20	MJ_{ex}/m^2a
Human-made	Occupation, heterogeneous, agricultural	23.20	MJ_{ex}/m^2a

Human-made	Occupation, industrial area	23.20	MJ_{ex}/m^2a
Human-made	Occupation, industrial area, benthos	0.00	MJ_{ex}/m^2a
Human-made	Occupation, industrial area, built up	23.20	MJ_{ex}/m^2a
Human-made	Occupation, industrial area, vegetation	23.20	MJ_{ex}/m^2a
Human-made	Occupation, mineral extraction site	23.20	MJ_{ex}/m^2a
Human-made	Occupation, pasture and meadow	23.20	MJ_{ex}/m^2a
Natural	Occupation, pasture and meadow, extensive	0.00	MJ_{ex}/m^2a
Human-made	Occupation, pasture and meadow, intensive	23.20	MJ_{ex}/m^2a
Human-made	Occupation, permanent crop	23.20	MJ_{ex}/m^2a
Natural	Occupation, permanent crop, extensive	0.00	MJ_{ex}/m^2a
Human-made	Occupation, permanent crop, intensive	23.20	MJ_{ex}/m^2a
Human-made	Occupation, sea and ocean	10.04	MJ_{ex}/m^2a
Natural	Occupation, shrub land, sclerophyllous	0.00	MJ_{ex}/m^2a
Human-made	Occupation, traffic area	23.20	MJ_{ex}/m^2a
Natural	Occupation, tropical rain forest, natural system	0.00	MJ_{ex}/m^2a
Human-made	Occupation, tropical rain forest, human-made system	23.20	MJ_{ex}/m^2a
Human-made	Occupation, unknown	23.20	MJ_{ex}/m^2a
Human-made	Occupation, urban	23.20	MJ_{ex}/m^2a
Human-made	Occupation, water bodies, artificial	23.20	MJ_{ex}/m^2a
Human-made	Occupation, water courses, artificial	23.20	MJ_{ex}/m^2a

10.2 SUPPORTING INFORMATION FROM THE MANUSCRIPT OF CHAPTER 3

10.2.1 Mathematical explanation for the indicator presented in this paper (S1)

$\Phi_{natural,\ i} = (SIAb_{natural,\ i}) + (NI_{natural,\ i}) - (PotNPP_i)$

$\Phi_{man\text{-}made,\ i} = (SIAb_{man\text{-}made,\ i}) + (N.I._{\ man\text{-}made,\ i}) + (HI_i) - (TBP_i)$

$(SIAb_{man\text{-}made,\ i}) = (SIAb_{natural,\ i}) \cdot \gamma_i$

$(NI_{man\text{-}made,\ i}) = (NI_{natural,\ i}) \cdot \lambda_i$

Therefore,

$\Phi_{man\text{-}made,\ i} = [(SIAb_{natural,\ i}) \cdot \gamma_i] + [(NI_{natural,\ i}) \cdot \lambda_i] + (HI_i) - (TBP_i)$

Now let us consider the system boundaries of this analysis as the Earth's boundaries, i.e., the solar irradiation will be taken out of it. Then, if we want to evaluate the variation in exergy lost (and destroyed) of a biomass production system, in comparison to the exergy lost (and destroyed) of a natural reference system, for the same land area, we have:

$$\Delta\Phi_i = \Phi_{man\text{-}made,\, i} - \Phi_{natural,\, i}$$

$$\Delta\Phi_i = [(NI_{natural,\, i} \,.\, \lambda_i) + (HI_i) - (TBP_i)] - [(NI_{natural,\, i}) - (PotNPP_i)]$$

$$\Delta\Phi_i = (NI_{natural,\, i} \,.\, \lambda_i) + (HI_i) - (TBP_i) - (NI_{natural,i}) + (PotNPP_i)$$

$$\Delta\Phi_i = [(NI_{natural,i}).(\lambda_i - 1)] + (HI_i) + (PotNPP_i) - (TBP_i)$$

Physically, the opposite of the exergy lost (and destroyed) is the exergy produced. So, the variation of exergy lost (and destroyed) is equal to the opposite of the variation of exergy produced:

$$\Delta\Phi_i = -\Delta EP_i$$

$$\boxed{\Delta EP_i = (TBP_i) - (HI_i) - (PotNPP_i) - [(NI_{natural,i}).(\lambda_i - 1)]}$$

If we consider:

$$\lambda_i \approx 1$$

$$\Delta EP_i = (TBP_i) - (HI_i) - (PotNPP_i) - [(NI_{natural,i}).(1 - 1)]$$

$$\Delta EP_i = (TBP_i) - (HI_i) - (PotNPP_i) - [(NI_{natural,i}).(0)]$$

$$\boxed{\mathbf{\Delta EP_i = (TBP_i) - (HI_i) - (PotNPP_i)}}$$

<u>Where:</u>

$\Phi_{natural,\, i}$ = Exergy lost (and destroyed) at a natural system, in a land area i. In both natural and man-made systems, this term considers the exergy that is not transformed to biomass, either by exergy destruction, according to the 2nd law of thermodynamics, or by exergy lost, which are flows that go out of the system boundaries, but not as biomass (e.g. evapotranspiration).

$\Phi_{man\text{-}made,\, i}$ = Exergy lost at a man-made system, in a land area i

$SIAb_i$ = Solar irradiation absorbed by the biomass, in a land area i

NI_i = Natural inputs consumed by the biomass, in a land area i

$PotNPP_i$ = Potential NPP, in a land area i

HI_i = Cumulative resources consumed, though inputs from men, by the man-made biomass production system, in a land area i

TBP_i = Total biomass produced by the man-made system, in a land area i

γ_i = Factor that represents the variation in the solar irradiation absorption between a man-made and the natural system, for the same land area i.

λ_i = Factor that represents the variation in the consumption of natural inputs between a man-made and the natural system, for the same land area i.

$\Delta\Phi_i$ = The variation in exergy lost (and destroyed) between a natural and a man-made system, in the same land area i.

ΔEP_i = The variation in exergy produced between a natural and a man-made system, in the same land area i. When this indicator is positive, it represents the amount of exergy produced due to that specific land use; and when negative, it represents the opposite.

10.2.2 Chemical composition of the crops from the case studies (biomass harvested and above-ground residues) and the respective chemical exergy value considered (S2)

Table 10.15: Exergy value considered for the chemical compounds and the chemical composition of the crops

Crop	Exergy value (MJ_{ex}/kgDM)	Potatoes		Wheat		Soybean		Maize		Sugarcane		Palm fruit		
Part of the crop	-	Tuber	Stem/ Leaves	Grain	Stem/ Leaves	Seeds	Stem/ Leaves	Ear/cob	Stover	Cane	Leaves	Fruit	Leaves	Trunk
Portion of total	-	89%	11%	17%	83%	18%	82%	20%	80%	89%	11%	33%	50%	17%
Moisture	-	78%	60%	20%	80%	10%	60%	21%	75%	67.5%	80.6%	26%	70%	50%
Cellulose (g)	18.54	3.85	65.00	11.15	32.60	17.00	65.00	4.75	37.30	22.30	38.70	10.10	47.50	45.00
Hemicellulose (g)	19.95	3.85	0.00	11.15	22.60	4.00	0.00	4.75	24.10	18.50	32.40	6.40	9.30	25.00
Sugars (g)	16.52	0.00	0.00	1.20	0.00	7.00	20.00	2.60	0.00	2.00	0.00	0.00	0.00	0.00
Sucrose (g)	17.55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	46.20	0.00	0.00	0.00	0.00
Starch (g)	18.54	72.50	20.00	56.00	0.00	0.00	0.00	71.70	0.00	0.00	0.00	0.00	0.00	0.00
Lignin (g)	29.13	0.00	10.00	2.40	16.90	1.00	10.00	0.00	17.50	3.90	7.10	4.70	16.40	18.00
Protein (g)	23.71	10.60	0.00	13.40	0.00	40.80	0.00	9.50	11.20	0.60	8.00	2.60	6.70	0.00
Oils (g)	39.55	0.00	0.00	1.25	0.00	17.90	0.00	2.15	0.00	0.00	0.00	74.50	0.00	0.00
Fats (g)	39.55	0.70	0.00	1.25	0.00	2.10	0.00	2.15	0.00	0.60	3.60	0.00	0.00	0.00
Minerals (g)	2.11	0.50	0.00	0.40	0.00	2.80	0.00	1.60	1.80	1.40	1.10	0.30	0.00	2.00
Ash (g)	2.11	5.40	0.00	1.90	10.20	6.00	0.00	1.40	6.10	1.70	8.90	1.40	8.30	0.00
Others (g)[a]	20.66	2.60	5.00	0.00	17.70	1.40	5.00	0.00	2.00	2.80	0.00	0.00	11.80	10.00
Total (g)	-	100.0	100.0	100.1	100.0	100.0	100.0	100.6	100.0	100.0	99.8	100.0	100.0	100.0

[a] It was considered an exergy value of the average of the other chemical compounds, since it was not specified what this component was.

10.3 SUPPLMENTARY MATERIAL FROM THE MANUSCRIPT OF CHAPTER 4

10.3.1 Life Cycle Impact Assessment (LCIA) of fossil-based PVC through several multi-criteria LCIA methods that allow single score results (SM-1)

We performed a cradle-to-gate life cycle assessment (LCA) of fossil-based PVC, by using the process called "*Polyvinylchloride, suspension polymerized, at plant/RER*" from ecoinvent database (Ecoinvent, 2010), and modeled it in Simapro 7.3. Then, we calculated the environmental pressure of this product through multi-criteria life cycle impact assessment (LCIA) methods that allowed the generation of single score results. We chose the following LCIA methods, available in ecoinvent database:

- Eco-indicator 99 H/A (European normalization factors)
- Recipe endpoint H/A (World normalization factors)
- Impact 2002+
- EPS 2000
- Ecological Scarcity 2006

The EDIP 2003 method is also a multi-criteria LCIA method that generates single score results, although we did not consider it in this analysis because it does not provide normalization and weighting factors for the resource categories.

In Figure 10.18 (a), we can see that the production of ethylene is responsible for more than half of the environmental impacts in Eco-indicator 99 H/A, Recipe endpoint H/A, Impact 2002+, and EPS 2000. In the Ecological Scarcity 2006 method, ethylene production was responsible for only 34% of the overall PVC production environmental impacts.

In Figure 10.18 (b), we can see that the impact categories related *resource depletion*[§§§] were responsible for more than 59% the environmental impacts for Ecoindicator 99 H/A, Recipe endpoint H/A, Impact 2002+, and EPS 2000. For Ecological Scarcity 2006, "emissions into air" is the environmental impact category with highest values. Global warming impact categories are also responsible for a considerable share in most LCIA methods, especially

[§§§] The resource depletion categories considered in Figure 1b are: (1) "Fossil fuel", for Ecoindicator 99 H/A; (2) "Fossil depletion", for Recipe endpoint H/A; (3) "Non-renewable energy", for Impact 2002+; (4) "Depletion of reserves", for EPS 2000; and (5) "Energy resources", for Ecological scarcity 2006.

Recipe endpoint H/A and Impact 2002+. EPS 2000 and Ecological Scarcity 2006 do not have a specific category for global warming, for that reason they had null values.

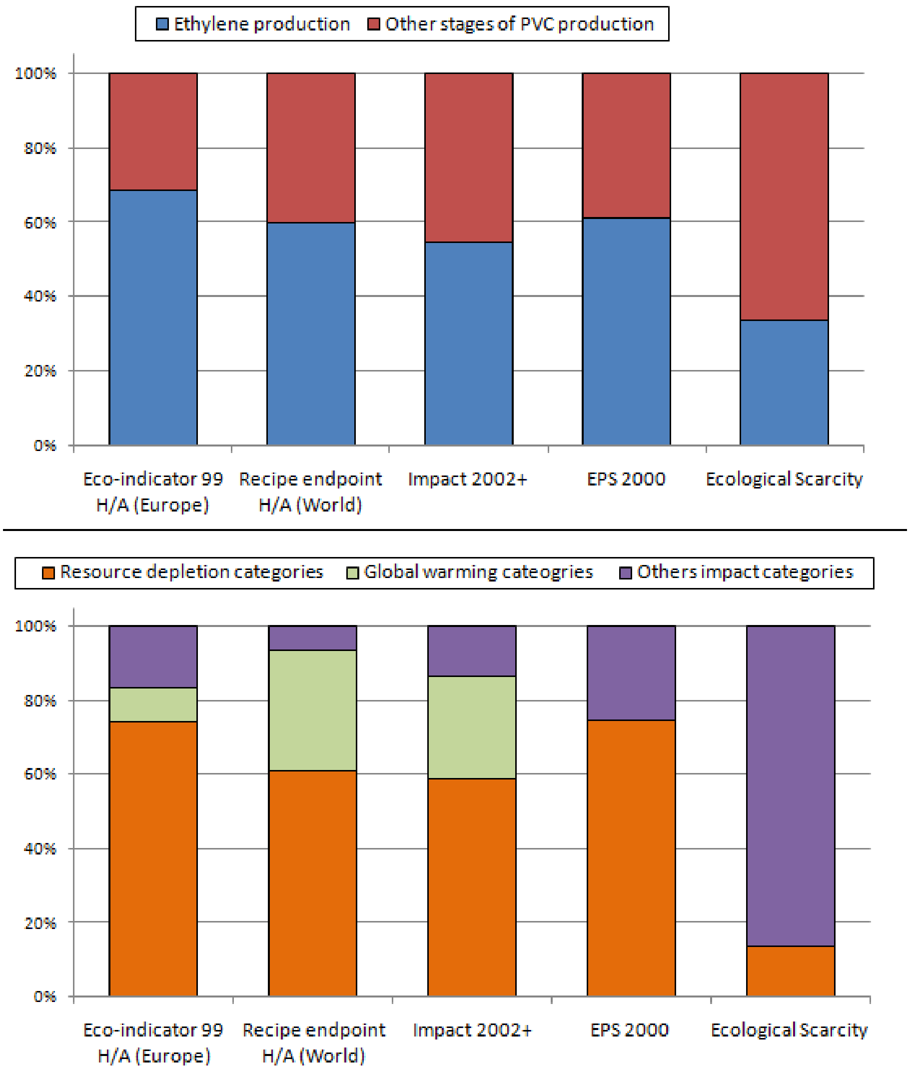

Figure 10.18: LCIA of the PVC from ecoinvent database, through several LCIA methods, showing the most striking phases ((a) – top) and the most striking environmental impact categories ((b) – below)

10.3.2 Life Cycle Inventory (LCI) of the bioethanol produced in Brazil (SM-2)

This section presents the Life Cycle Inventory (LCI) of the bioethanol produced from sugarcane, in Brazil. The data was based on literature review, regarding the state of Sao Paulo, the biggest producer from that country.

The replacement of fossil-based to bio-based feedstock is still in its initial phases, and comparing these two feedstocks may give misleading interpretations since the fossil-based feedstock has an established and mature technology while the bio-based feedstock is in its initial stage with room for improvement. For this reason, in our research we considered two scenarios: the first, “Scenario 1”, referred to present data, from 2010; and the second, “Scenario 2”, referred to a prognosis of data for the future, for 2018, with technological advances. In this section we present the LCI of both scenarios.

10.3.2.1 Scope

This study was a cradle-to-gate analysis of Brazilian bioethanol, but with specific data from the state of São Paulo, the biggest bioethanol producer from Brazil. According to Macedo et al. (2008) the rotation of sugarcane crop can be every 6 years, with 5 cuts. The first cycle of sugarcane is called *plant cane*, and lasts approximately 1.5 years. The following cycles are called *ratoon*, last 1 year, and have lower yields. The crop cycles can vary, but in this study we considered the same from Macedo et al. (2008), i.e. with a time length of 6 years, 1 cut of plant cane, and 4 cuts of ratoon.

We divided this analysis in two main processes: (1) Sugarcane production (or agricultural phase); (2) Bioethanol production, at the mill (or industrial phase). The reference flow considered was 1,000 kg of sugarcane produced, taken to the bioethanol mill, and used exclusively for production of hydrous bioethanol (95%); therefore, in an “autonomous distillery”. Figure 10.19 represents the bioethanol system boundaries.

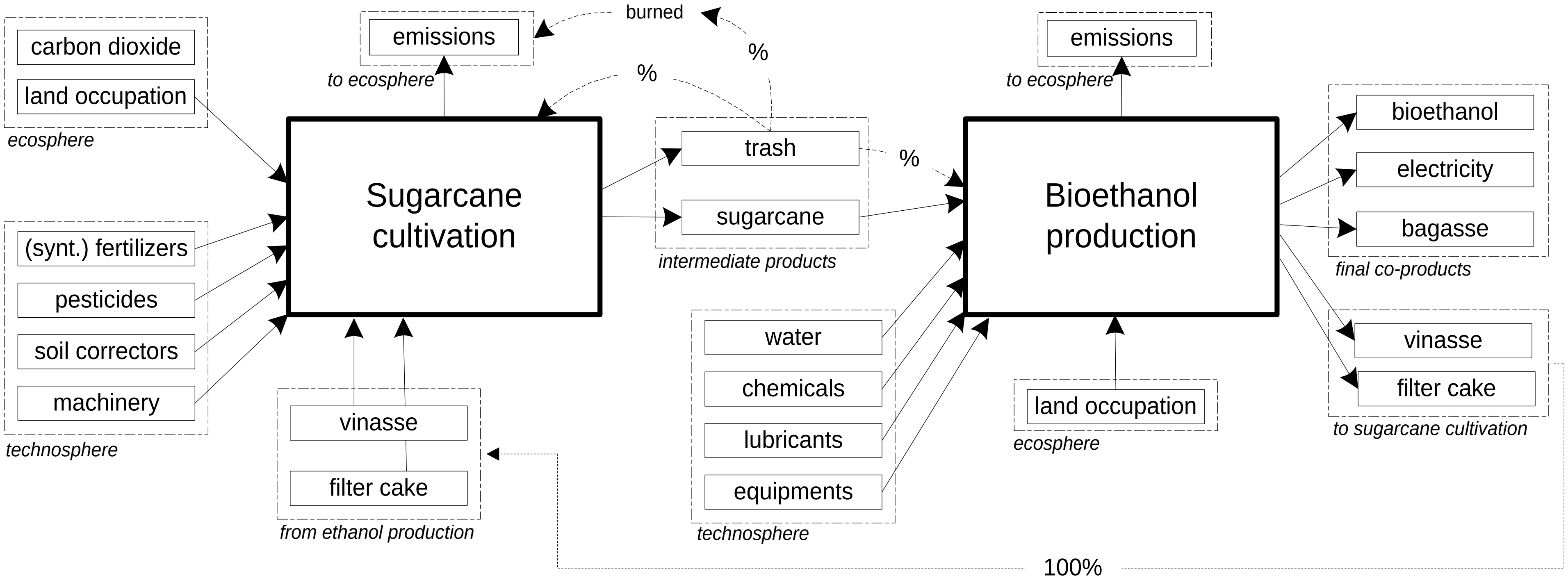

Figure 10.19: System boundaries and simplified flowchart of the bioethanol (from sugarcane) system

10.3.2.2 Assumptions

Before performing the data collection, some assumptions needed to be made.

a) Characteristics of sugarcane, bagasse, and trash

Whenever was necessary, the chemical characteristics of the sugarcane was based on Brehmer (2008), and of the bagasse and the trash were based on Seabra (2008).

b) Biomes where the sugarcane is cultivated

The bioethanol and sugarcane were considered to be produced in the state of Sao Paulo. For more specific spatial data, we considered the four biggest sugarcane producer *mesoregions* (IBGE, 2011) from the state of São Paulo, until 2010: Ribeirão Preto, São José do Rio Preto, Araçatuba, and Bauru. These *mesoregions* are responsible for approximately 65% of the sugarcane production from the state of São Paulo and more than 38% of the Brazilian production.

Those four *mesoregions* together have 52.77% of their territory in the *Cerrado* biome, and 47.23% in the Atlantic Forest biome.

c) Productivity of sugarcane

For this input we considered the average data of the four biggest producing *mesoregions* (IBGE, 2011) from the state of São Paulo, weighted to their share of sugarcane production for the years 2006 until 2010: Ribeirão Preto, São José do Rio Preto, Araçatuba, and Bauru.

In Scenario 1, the sugarcane productivity was based on the values for 2010 from those four *mesoregions* according to IBGE (2011). For Scenario 2 we considered that the productivity increased. To make a prognosis on the increase of sugarcane productivity, we tried to base on literature information. Goldemberg and Guardabassi (2010) gave a growth rate of 4%/year in the yield of bioethanol, taking into account the last 35 years. They suggested also that this increase was evenly distributed by the sugarcane productivity and the bioethanol yield, therefore, giving an increase of 1.98%/year for sugarcane productivity. Gauder et al. (2011) gave a growth rate of 2.1%/year of bioethanol yield, taking into account the last 20 years. If we assume what Goldemberg and Guardabassi (2010) have stated before, we can presume a growth of 1.04%/year only in the sugarcane productivity. At Macedo et al. (2008), for their prognosis for 2020 (with a sugarcane productivity of 95 ton/ha), they assumed a growth rate of 0.62%/year. In this study we wanted to be more conservative than the previous work, assuming a slightly lower growth rate, of 0.60%/year. Therefore, the productivity of sugarcane for scenario 2, which is set to happen eight years later than scenario 1, was considered to be 4.9% higher. The data on the productivity of the four *mesoregions*, and their weighted average, for both scenarios, can be seen in Table 10.16.

Table 10.16: Specific geographical data for solar irradiation, effective rainfall, and sugarcane productivity in the state of São Paulo, Brazil.

Mesoregion	Share of total (%)	Productivity in 2010 (scenario 1) (ton/ha)	Productivity in 2018 (scenario 2) (ton/ha)
Ribeirão Preto	43.8	86.25	-
São José do Rio Preto	24.0	87.20	-
Araçatuba	15.1	87.49	-
Bauru	17.1	82.89	-
Total	100.0	-	-
Weighted average (SP)	-	86.09	90.31

d) Land use change (LUC)

The evaluation of LUC may be performed by the "direct" LUC (dLUC) and the "indirect" LUC (iLUC). The latter is the LUC that occurs not in the same area where the crop was produced, but induced by the direct LUC.

For the dLUC, we considered the same four *mesoregions* of the state of Sao Paulo. According to Rudorff et al. (2010), at those four *mesoregions*, the expansion of sugarcane cultivation occurred at pasture land (66.8%), at arable land from other crops (30.6%), at permanent crop land (citrus) (2.2%), and also at natural vegetation areas (0.4%), between the years 2003 and 2009. This dLUC occurred only in 15.54% of the total sugarcane area from those four *mesoregions* on 2009, i.e., the other 84.46% were area where sugarcane was already cultivated before 2003. According to the Renewable Energy Directive from the European Union (Eurpean Union, 2009), the impacts on greenhouse gases from dLUC should be annually normalized by equally dividing it over 20 years.

For the iLUC, there is no consensus in the scientific community among models to calculate their values and is not considered in this document, which is aimed for an attributional LCA.

e) Vinasse and Filter cake application

Vinasse and Filter cake are co-products from the bioethanol production. They are commonly used in the sugarcane fields as source of nutrients. We sought to have a dosage of 150m^3/ha of vinasse and 6t/ha of filter cake, values commonly used in the state of São Paulo. Also, we wanted to use all the vinasse and filter cake produced in the bioethanol mill on the sugarcane fields. So, considering the amount produced, we obtained the share of area where the vinasse and filtercake would be applied. We considered a production of 12.5 L vinasse / L bioethanol, and 12 kg of filter cake / ton of sugarcane (Macedo, 2005).

f) Synthetic fertilizers use

The amount of N, P_2O_5, and K_2O needed in the sugarcane fields was assumed to be equal to what was published in Macedo (2005). The concentration of these chemical compounds in the vinasse and filter cake was also considered from the same source. So, to obtain the final average consumption of synthetic fertilizers, we subtracted the total value needed from the amount available in the vinasse and filter cake applied. The vinasse was considered to be applied in both plant cane and ratoon, while the filter cake was considered to be applied only in the plant cane. The values published in Macedo (2005) for amount of N, P_2O_5, and K_2O needed for sugarcane cultivation, and their quantity available in vinasse and filter cake can be seen in Table 10.17.

Table 10.17: Amount of N, P_2O_5, K_2O needed in the sugarcane fields (plant cane and ratoon) and available in the vinasse and filter cake produced in the bioethanol mill.

	Amount of nutrients needed in:		Amount of nutrients available on:	
	Plant cane (kg/ha)	Ratoon (kg/ha)	Vinasse (kg/m^3 vinasse)	Filter cake (g/kg filter cake)
N	50	100	0.305	12.50
P_2O_5	120	30	0.295	21.80
K_2O	120	130	1.505	3.20

g) Harvest of sugarcane

The harvest of sugarcane in Brazil can be performed manually or mechanically, making use of fire or not. Due to legislation (Governo do Estado de Sao Paulo, 2002) and an agro-environmental protocol for the sugar and bioethanol sector (UNICA, 2007), the unburned harvest is expected to be in 100% of the sugarcane fields in the state of São Paulo sometime between 2017 and 2031. From Macedo et al. (2004) and Seabra et al. (2011) data on sugarcane harvest, which used 2002 and 2008 as reference years, respectively, we see a trend of increasing mechanical harvest in 2%/year, and decrease of pre-burning harvest of 1.7%/year. Keeping this trend for 2010, we have 52% of mechanical harvest and 62% of pre-burned harvest, which were used in our scenario 1 (in Seabra et al. (2011) the values were 48% and 65%, respectively).

For scenario 2 (with reference year 2018), we considered that just 20% of the producers would be following the agro-environmental protocol (0% with pre-burning harvest), and 80% would be following the legislation (20% with burning harvest), therefore considering a value of 16% burned harvest. We assumed that the manual harvest is not economic feasible for unburned areas, therefore it should not be higher than 16%. For this reason, we considered 85% of mechanical harvest and 15% of manual harvest.

The values considered in this study for burned and unburned harvest for scenario 2 may be considered conservative, if we consider the data from literature. At Novaes et al. (2011), a prescriptive model (using expert knowledge) estimated a value between 81% and 92% of unburned harvest, for the state of Sao Paulo, for the year of 2014; i.e., four years before the reference year of scenario 2.

h) Fuel use

For accounting the amount of diesel consumed in the sugarcane cultivation we based on data from Macedo et al. (2004) with some updates from Macedo et al. (2008). We considered the average distance between the sugarcane field and the bioethanol mill of 23 km, and an average distance between the synthetic fertilizers and the sugarcane field of 20 km. For scenario 2, to account for the transportation of trash to the bioethanol mill, we adopted the same methodology for transportation of sugarcane to the bioethanol mill. The extra amount of diesel needed to a possible mechanical trash blanketing was not considered due to lack of data.

i) Water use

The sugarcane cultivation is performed without irrigation; therefore we considered no consumption of water at the agricultural stage.

In the bioethanol mill, we based our data on Ometto (2005) and Ometto et al. (2009), and considered the water consumption for washing the sugarcane from burned harvest, for cooling equipments, imbibitions, washing the fermentation vat, and for heat exchange for the electricity generator.

j) Outputs from the bioethanol mill

For the production of bioethanol, bagasse, and electricity, we considered the parameters from Macedo et al. (2008), using the values for the year 2005/2006 for our scenario 1, and the values for the scenario 2020 for our scenario 2.

In the scenario 2020 from Macedo et al. (2008), it is considered that the trash recovery for electricity generation is 40%. From their considerations (95 ton cane/ha and trash production equals to 14% of the cane produced), the amount of trash taken to the mill was 5.32 ton/ha. In order to use the same values as electricity output from the bioethanol mill, we have to consider the same amount of trash going in the bioethanol mill. Since our values of productivity and amount of trash produced are different, the amount of trash taken to the mill will be different from 40% (it was equal to 47%).

k) Other data for the LCI

For equipments and land occupation in the bioethanol mill, we used the data from Macedo et al. (2008), but considering the amount needed to produce the bioethanol from our reference flow (1,000 kg of sugarcane). In the aforementioned publication, it was quantified the total area and equipments needed in a bioethanol mill, but not the value per unit of bioethanol produced as shall be calculated here. For the equipments, we considered a lifetime of 24 years.

The other inputs needed in the production of sugarcane and bioethanol were collected directly from literature.

l) Emissions from the sugarcane field

We divided the emissions from the sugarcane field in three groups:

- Emissions from the machinery that consumed diesel (e.g., tractors). For this, we calculated the emissions based on the diesel consumption, using the emission factors from EEA (2006) and Nemecek and Kagi (2007);
- Emissions from the trash burned during harvest, which we calculated based on the emission factors from EEA (2009) and IPCC (2006a) (there were not emission factors specific for sugarcane trash, so we used data for burning of agricultural residues);
- Soil emissions, in which we considered the emissions of CO_2 (to air), N_2O (to air), NH_3 (to air), NO_x (to air), NO_3 (to ground water), P (to surface water), and pesticides (to soil). We calculated the values from the approaches presented in IPCC (2006b), Nemecek and Kagi (2007), Jungbluth et al. (2007), Andrade et al. (2011), Bloesch et al. (1997), and Dijkman et al. (2012).

m) Emissions from the bioethanol mill

We divided the emissions from the bioethanol mill in three groups:

- Emissions from the biomass burned to generate power and electricity. In scenario 1, only bagasse is burned, while in scenario 2 a portion of the trash from the sugarcane field is also burned. For bagasse, we based our data on the emission factors published in Silva (2000). For trash, we based on the same source, but transformed the emission factors from bagasse to trash, considering their dry matter and carbon content.
- The carbon dioxide emitted in the bioethanol fermentation was calculated through stoichiometry (0.957 gCO_2/gEtOH);
- Other emissions, which we considered the organic matter sent to water (BOD_5) from Macedo (2005), and the emission of sulfuric acid, also to water, based on the approach from Ometto et al. (2009).

n) Carbon balance

In order to ensure the quality of the data collected, we performed a biogenic carbon balance within the system boundaries of the system (Figure 10.19). From the amount of carbon present in the sugarcane and the trash, according to Brehmer (2008) and Seabra (2008) respectively, we estimated how much carbon dioxide was absorbed by the plant. We did not account for the carbon uptake of the trash left on the field. From the total carbon uptake we subtracted the emissions of biogenic carbon and the amount of carbon that was going out of the system as bioethanol. The amount of carbon left was considered to be present in the vinasse and filter cake or as not previously accounted, and was named "*Carbon dioxide, biogenic, from other sources*". We considered the amount of carbon present in the bagasse leaving the system, at scenario 1, as a biogenic emission due to the accounting of their uptake beforehand.

10.3.2.3 Life Cycle Inventory (LCI)

First, we present the main differences in the two scenarios that caused the further differences in the Life cycle inventory (LCI).

Table 10.18: Parameters for each scenario

	Scenario 1	**Scenario 2**
Sugarcane productivity	86.09 ton/ha	90.31 ton/ha
Manual harvest	48%	15%
Mechanical harvest	52%	85%
Pre-burned harvest	62%	16%
Unburned harvest	38%	84%
Area with vinasse application	60%	68%
Area with filter cake application	83%	89%

Trash burned	62%	16%
Trash left on the field	38%	37%
Trash taken to the mill (used for electricity generation)	0%	47%
Bioethanol yield*	86.3 L/ton	92.3 L/ton
Bagasse used for electricity generation*	90.4%	100%
Technology for electricity generation*	*Cogeneration*, steam at 2.1 MPa and 300°C	*Condensing extraction steam turbine*, steam at 6.5 Mpa and 480°C

* Based on Macedo et al. (2008)

The LCI of bioethanol for the two scenarios can be seen in the tables below.

Table 10.19: LCI of 1,000 kg of sugarcane produced

	Scen. 1	Scen. 2	Unit	Source
CO_2 captured, by sugarcane	568.43	568.43	kg	Based on: Brehmer (2008); Phyllis (2011); Seabra (2008)
CO_2 captured, by trash (leaves)	95.69	97.26	kg	Based on: Brehmer (2008); Phyllis (2011); Seabra (2008)
Land occupation	143.39	136.50	m^2a	IBGE (2011) and based on Macedo et al. (2008)
Land transf., from pasture	0.74	0.71	m^2	(Rudorff et al., 2010)
Land transf., from arable	0.34	0.32	m^2	(Rudorff et al., 2010)
Land transf., from perm. crop	0.02	0.02	m^2	(Rudorff et al., 2010)
Land transf., from Atl. forest	0.00	0.00	m^2	(Rudorff et al., 2010)
Land transf., from “cerrado”	0.00	0.00	m^2	(Rudorff et al., 2010)
Land transf., to arable	1.11	1.06	m^2	(Rudorff et al., 2010)
Diesel consumption	1.79	2.00	kg	Based on: Macedo et al. (2008); Macedo et al. (2004)
N – nitrogen (Urea)	0.71	0.64	kg	Based on: Macedo et al. (2008); Macedo et al. (2004)
P_2O_5	0.16	0.12	kg	Based on: Macedo et al. (2008); Macedo et al. (2004)
K_2O	0.60	0.46	kg	Based on: Macedo et al. (2008); Macedo et al. (2004)
Filter cake	12.00	12.00	kg	Based on: Macedo (2005)
Vinasse	1.08	1.15	m^3	Based on: Macedo (2005)
Limestone	4.54	4.32	kg	(Macedo et al., 2008)
Pesticide (atrazine/gliphosate)	31.46	29.95	g	(Macedo, 2005)
Pesticide (carbofuran)	1.61	1.53	g	(Macedo, 2005)
Pesticide (others)	0.57	0.55	g	(Macedo, 2005)
Tractors, harvesters	0.10	0.10	kg	Based on: Macedo et al. (2008)
Implements	0.03	0.03	kg	Based on: Macedo et al. (2008)
Trucks	0.20	0.19	kg	Based on: Macedo et al. (2008)
Cane (taking out “seeds”)	1,000.00	1,000.00	kg	Based on: IBGE (2011); Macedo et al. (2008); Macedo et al. (2004)
Trash	129.07	128.90	kg	Ronquim (2007)
Trash burnt	80.02	20.62	kg	Based on: Ronquim (2007)
Trash left of the field	49.05	47.69	kg	Based on: Ronquim (2007)
Trash taken to the mill	0.00	60.58	kg	Based on: Macedo et al. (2008); Ronquim (2007)

Table 10.20: LCI of bioethanol produced from 1,000 kg of sugarcane

	Scenario 1	Scenario 2	Unit	Source
Cane	1,000.00	1,000.00	kg	Based on: IBGE (2011) and Macedo et al. (2008)
Trash	0.00	60.58	kg	Based on: Ronquim (2007); Macedo et al. (2008)
Land occupation	0.01	0.01	m^2a	Based on: Macedo et al. (2008)
Equipments	0.20	0.20	kg	Based on: Macedo et al. (2008)
Water	5,642.76	4,798.76	kg	Based on: Ometto (2005) and Ometto et al. (2009)
H_2SO_4	0.64	0.68	kg	(Seabra et al., 2011)
CaO	0.88	0.88	kg	(Seabra et al., 2011)
NaOH	0.25	0.26	kg	(Seabra et al., 2011)
Lubrificants	0.01	0.01	kg	(Seabra et al., 2011)
Bioethanol	86.30	92.30	L	(Macedo et al., 2008)*
Electricity (leaving the system)	9.20	135.00	kWh	(Macedo et al., 2008)*
Bagasse (not consumed)	26.88	0.00	kg	(Macedo et al., 2008)*
Vinasse	1.08	1.15	m^3	(Macedo, 2005)
Filter cake	12.00	12.00	kg	(Macedo, 2005)

* For scenario 1 we considered the values for 2005/2006; for scenario 2 we considered the values for 2020.

Table 10.21: Field emissions, for 1,000 kg of sugarcane produced

Substance	From	To	Scenario 1	Scenario 2	Unit	Source
CO_2	Direct land transformation	Air	3.73	3.55	kg	(Eurpean Commission, 2010); (Eurpean Union, 2009)
As	Biomass	Air	3.28	0.84	mg	(EEA, 2009)
Cd	Biomass	Air	2.77	0.71	mg	(EEA, 2009)
CH_4	Biomass	Air	152.54	39.31	g	(IPCC, 2006a)
CO	Biomass	Air	5.20	1.34	kg	(IPCC, 2006a)
CO_2	Biomass (trash burned)	Air	85.59	22.06	kg	(IPCC, 2006a)
Cr	Biomass	Air	12.43	3.20	mg	(EEA, 2009)
Hg	Biomass	Air	0.45	0.12	mg	(EEA, 2009)
N_2O	Biomass	Air	3.95	1.02	g	(IPCC, 2006a)
NH_3	Biomass	Air	135.59	34.94	g	(EEA, 2009)
Ni	Biomass	Air	10.00	2.58	mg	(EEA, 2009)
NMVOC	Biomass	Air	355.92	91.73	g	(EEA, 2009)
NO	Biomass	Air	67.79	17.47	g	(EEA, 2009)
NO_x	Biomass	Air	141.24	36.40	g	(IPCC, 2006a)
Pb	Biomass	Air	48.87	12.59	mg	(EEA, 2009)
PM_{10}	Biomass	Air	327.68	84.45	g	(EEA, 2009)
$PM_{2,5}$	Biomass	Air	310.73	80.08	g	(EEA, 2009)
Se	Biomass	Air	2.03	0.52	mg	(EEA, 2009)
SO_x	Biomass	Air	16.95	4.37	g	(EEA, 2009)
Total PAHs	Biomass	Air	6.11	1.57	g	(EEA, 2009)
TSP	Biomass	Air	327.68	84.45	g	(EEA, 2009)
Zn	Biomass	Air	1.58	0.41	mg	(EEA, 2009)
Benz(a)-Anthracene	Diesel	Air	0.14	0.16	mg	(EEA, 2006)

Benzene	Diesel	Air	13.08	14.63	mg	(Nemecek and Kagi, 2007)
Benzo(a)pyrene	Diesel	Air	0.05	0.06	mg	(EEA, 2006)
Benzo(b)-Fluor-anthene	Diesel	Air	0.09	0.10	mg	(EEA, 2006)
Cd	Diesel	Air	0.02	0.02	mg	(EEA, 2006)
CH_4	Diesel	Air	0.30	0.34	g	(EEA, 2006)
Chrysene	Diesel	Air	0.36	0.40	mg	(EEA, 2006)
CO	Diesel	Air	28.68	32.06	g	(EEA, 2006)
CO_2	Diesel	Air	5.59	6.25	kg	(Nemecek and Kagi, 2007)
Cr	Diesel	Air	0.09	0.10	mg	(EEA, 2006)
Cu	Diesel	Air	3.05	3.41	mg	(EEA, 2006)
Dibenzo (a,h)-Anthracene	Diesel	Air	0.02	0.02	mg	(EEA, 2006)
Fluoranthene	Diesel	Air	0.81	0.90	mg	(EEA, 2006)
N_2O	Diesel	Air	2.31	2.58	g	(EEA, 2006)
NH_3	Diesel	Air	0.01	0.01	g	(EEA, 2006)
Ni	Diesel	Air	0.13	0.14	mg	(EEA, 2006)
NMVOC	Diesel	Air	13.03	14.57	g	(EEA, 2006)
NO_x	Diesel	Air	90.16	100.79	g	(EEA, 2006)
Phenanthene	Diesel	Air	4.48	5.01	mg	(EEA, 2006)
PM	Diesel	Air	7.04	7.87	g	(EEA, 2006)
$PM_{2,5}$	Diesel	Air	6.63	7.41	g	(EEA, 2006)
Se	Diesel	Air	0.02	0.02	mg	(EEA, 2006)
SO_2	Diesel	Air	1.81	2.02	g	(Nemecek and Kagi, 2007)
Zn	Diesel	Air	1.79	2.00	mg	(EEA, 2006)
CO_2	Soil	Air	3.12	2.91	kg	(IPCC, 2006b)
N_2O	Soil	Air	38.56	37.54	g	(IPCC, 2006b)
NH_3	Soil	Air	294.01	295.88	g	(Nemecek and Kagi, 2007)
NO_x	Soil	Air	8.10	7.88	g	(Nemecek and Kagi, 2007)
Atrazine	Soil	Air	0.26	0.25	g	(Dijkman et al., 2012)
Carbofuran	Soil	Air	0.01	0.01	g	(Dijkman et al., 2012)
Glyphosate	Soil	Air	0.07	0.07	g	(Dijkman et al., 2012)
Atrazine	Soil	Water (ground)	3.16	3.00	g	(Dijkman et al., 2012)
Carbofuran	Soil	Water (ground)	0.01	0.01	g	(Dijkman et al., 2012)
Glyphosate	Soil	Water (ground)	1.94	1.85	g	(Dijkman et al., 2012)
NO_3	Soil	Water (ground)	17.83	16.03	g	(Jungbluth et al., 2007)
Atrazine	Soil	Water (surface)	0.06	0.06	g	(Dijkman et al., 2012)
Carbofuran	Soil	Water (surface)	0.00	0.00	g	(Dijkman et al., 2012)
Glyphosate	Soil	Water (surface)	0.06	0.06	g	(Dijkman et al., 2012)
P (erosion)	Soil	Water (surface)	9.44	7.13	g	(Andrade et al., 2011)
P (run-off)	Soil	Water (surface)	20.77	20.10	g	(Bloesch et al., 1997)

Table 10.22: Emissions in the production of bioethanol (FU = 1,000 kg of sugarcane entering the system)

Substance	**From**	**To**	**Scenario 1**	**Scenario 2**	**unit**	**Source**
PM_{10}	Biomass burning	Air	40.16	60.46	g	(Silva, 2000)
NO_X	Biomass burning	Air	133.87	201.53	g	(Silva, 2000)
PAH	Biomass burning	Air	0.11	0.17	g	(Silva, 2000)

CO_2	Biomass burning	Air	174.03	261.99	kg	(Silva, 2000)
CO_2	Biogenic, present in the bagasse	Air	21.89	0.00	kg	Primary data
CO_2	Biogenic, from other sources	Air	177.14	169.91	kg	Primary data
CO_2	Fermentation	Air	65.13	69.66	kg	Primary data
BOD_5	Others	Water	0.20	0.20	kg	(Macedo, 2005)
H_2SO_4	Others	Water	0.64	0.68	kg	(Ometto et al., 2009)

10.3.3 Detailed analysis on the results from the climate change category (SM-3)

As additional information on the life cycle impact assessment on climate change, of the three scenarios of PVC resin, we present in this section their absolute values (Table 10.23), divided by source of emission and uptake of CO_2.

Table 10.23: Carbon footprint of the cradle-to-gate analysis of 1 kg PVC, separated by origin of emissions and uptake of carbon dioxide

Climate change (kg CO_2 eq.)	**Bioethanol-based PVC (2010)**	**Bioethanol-based PVC (2018)**	**Fossil-based PVC (2010)**
Uptake of CO_2	-8.92E+00	-7.84E+00	-2.23E-02
Biogenic emissions	7.54E+00	6.45E+00	7.38E-02
Fossil emissions	1.12E+00	1.06E+00	1.36E+00
CO_2 emissions due to dLUC	1.61E-01	1.52E-01	1.03E-01
Total net emissions	-9.31E-02	-1.89E-01	1.52E+00

The uptake of CO_2 and the biogenic emissions are higher in the bioethanol-based PVC (2010) than in bioethanol-based PVC (2018) due to higher efficiencies in electricity production (different allocation values) and bioethanol production, i.e., in the former scenario more sugarcane was needed to produce the same amount of bioethanol, since in the scenario from 2018 a higher efficiency is assumed in the bioethanol mill (92.3L/ton). The carbon stored in the PVC resin is the same in both scenarios, though (3.84E-01 kgC/kgPVC).

We can notice that in the bioethanol-based PVC scenarios, the fossil emissions and the CO_2 emissions due to dLUC were compensated by the amount of carbon absorbed and stored in the PVC resin; therefore, producing negative values in the total net emissions at those two scenarios.

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