1
Application of Life Cycle Assessment to Green Chemistry Objectives

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1.1
Introduction

Green chemistry (GC) is described by the 12 principles of green chemistry to guide the design of chemical products and processes that reduce or eliminate the generation and use of hazardous substances [1]. The guiding principles have been criticized for being qualitative and failing to provide an objective means to assess the overall "greenness" of proposed solutions or to evaluate trade-offs among conflicting principles, for example, reduced toxicity, but increased energy consumption [2]. Life cycle assessment (LCA) is the "compilation and evaluation of the inputs, outputs, and the potential environmental impacts of a product system" and provides a quantitative method to address these concerns (3], p.2). It is an international standard recognized as an effective methodology to evaluate improvement strategies and avoid shifting problems to other times and places or among various environmental media [4,5].

LCA, however, has its own set of limitations and unresolved methodology issues [6,7]. Some are particularly relevant to green chemistry, such as limited data for chemical production chains, lack of geographic specificity, and aggregation of emissions over time [8–10]. Increasingly, researchers are recognizing that the strengths and weaknesses of GC and LCA are complementary and are advocating for more effective integration of both methodologies to develop more sustainable solutions [2,11,12]. Anastas and Lankey (11], p.289) broaden the definition of green chemistry by considering chemistry to include "the structure and transformation of all matter" and hazardous impacts to address the "full range of threats to human health and the environment." Application of LCA to GC problems promises a better understanding of the flow of toxics through the economy and provides a robust framework for organizing knowledge about inherent hazards associated with product systems [13].

LCA is comprised of four basic steps [3]. *Goal and scope* identifies the purpose of the study, how the results will be used, and intended audience to whom the

Handbook of Green Chemistry Volume 10: Tools for Green Chemistry, First Edition. Edited by Evan S. Beach and Soumen Kundu.

results will be communicated. Clear definition of the decision context is critical to ensure the study provides objective information that enables the study commissioner and intended audience to make informed choices according to their values and priorities. *Life cycle inventory* (LCI) gathers data necessary to model mass and energy flows across the entire product system, from extraction or harvest of resources to the ultimate disposal of the product. Realistically, these models are always incomplete and a key decision is where to draw the boundaries on what is included in the system model. *Life cycle impact assessment* (LCIA) evaluates the significance of exchanges between the product system and the natural environment. Environmental interchanges are grouped, or classified into impact categories, such as acidification, climate change, human toxicity, or resource depletion. The inventory items for each impact category are then characterized for potency and mass, often in terms of a reference substance. For example, different greenhouse gases have different warming potentials, and are converted to an equivalent mass of CO_2, allowing the aggregated emission to be expressed as $CO_{2(e)}$ (equivalents). Finally, *interpretation* attempts to make sense of the analytical results to provide conclusions and recommendations necessary to satisfy the intended goal and scope of the study. For additional background on LCA methods relevant to GC, the reader is referred to previous reviews. Kralisch *et al.* [12] provides a general overview of LCA, specific considerations to be considered in chemical design, and examples of applications to emerging research problems. Tufvesson *et al.* [9] reviews “green chemistry” LCA studies to identify key parameters and methodological issues.

Principles of Green Chemistry

1) Prevention
2) Atom economy
3) Less hazardous chemical syntheses
4) Designing safer chemicals
5) Safer solvents and auxiliaries
6) Design for energy efficiency
7) Use of renewable feedstocks
8) Reduce derivatives
9) Catalysis
10) Design for degradation
11) Real-time analysis for pollution prevention
12) Inherently safer chemistry for accident prevention

The present chapter is intended to provide guidance on the effective integration of LCA methods into GC initiatives. It is assumed that the primary audience is a practitioner in green chemistry, familiar with the 12 principles of green chemistry, and perhaps with only a basic understanding of LCA methods.

(Because the principles are sometimes listed differently, the American Chemistry Society version is reproduced in the text box.)[1] There is no attempt to provide a comprehensive review of current state of the art in green chemistry progress or of the latest developments in LCA. Illustrative case studies or research results are presented to emphasize key points in the application of LCA methods to GC objectives. The chapter is organized based on grouping GC objectives into the following three overarching categories:

- Substitution of hazardous chemicals with safer alternatives (Principles 3,4,5,10,11,12).
- Design of processes to be more energy and material efficient (Principles 1,2,6,8,9,11).
- Promoting a transition to renewables (materials and energy) (Principles 6,7).

Further, Sjöström [14] characterized GC as a meta-discipline and described a classification model of GC research, management, and policy activities. Thus, the applicability of LCA to these various activities is also addressed for the various GC objectives.

Section 1.2 on substitution addresses the challenge of quantifying the toxicity of chemicals and the products and processes that depend on those chemicals. There are fundamental differences between LCA and GC or chemical alternative assessments. While these are typically focused on use of a chemical to provide a required function in a specific application, LCA considers use of the chemical (along with other chemicals) in a product system designed to satisfy some end user need or function. Thus, the two methodologies are designed to answer different questions, and this must be considered in the application of LCA to quantify toxicity concerns. Section 1.3 on greener processes builds on this introduction to consider a broader range of environmental impacts to assess trade-offs among the various GC principles and evaluate the overall greenness of a product or process. LCA provides a robust method to quantitatively compare alternative solutions, but does not provide guidance on development of alternatives. GC complements LCA by providing specific guidance to address the issues identified in the study. Section 1.4 addresses the broad goal of promoting renewable materials and energy. This class of problems extends system considerations to include a wide range of environmental impacts and dynamic effects, such as indirect land use changes that go well beyond traditional GC assessments. Given the importance of climate change concerns, determining whether renewables provide a real benefit over synthetic alternatives is a critical area for future work. Finally, Section 1.5 concludes with recommendations to promote the effective integration of LCA and GC to develop more sustainable business practices.

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1) Source: http://www.acs.org/content/acs/en/greenchemistry/what-is-green-chemistry/principles/12-principles-of-green-chemistry.html accessed Nov. 2015).

1.2
Substitution of Safer Chemicals

A variety of chemical alternative assessment procedures have been developed to guide selection of safer substitutes [15–17]. These methods typically begin with identifying a target chemical of concern followed by an analysis of the uses of the chemical. Virtually all methods advocate "life cycle thinking," but the focus on a specific chemical can narrow the problem definition. Alternatives are identified based on satisfying the same technical requirements for the application, or use under consideration. LCA, by contrast, has traditionally been focused on product systems and the function or service provided to the customer or end user. This broader perspective can inspire innovative approaches to satisfy the end user demand with an alternative solution that does not rely on the chemical of concern, thus eliminating the need for an alternatives assessment. If the assessment cannot identify an alternative that satisfies the technical requirements, then the analyst is advised to implement best practices to limit human exposures and environmental releases and to continue to research alternatives.

The use of comprehensive LCA studies in early development stages is often dismissed as being overly complex and time and effort intensive [12]. Problems gathering inventory data for chemicals, and particularly for fine chemicals have been well documented [9,18]. Inventory data is often protected as proprietary business information. Fine chemicals tend to be produced in smaller batches, comprised of many processing steps, and produced in shared equipment in multiproduct facilities, with much data collected only at the facility level. A case study comparing alternative assessment tools for the characterization of organic solvents concluded use of LCA was limited due to data constraints that included both inventory data for the production of chemicals and characterization factors for toxicity of chemicals [19].

1.2.1
Missing Inventory Data and Characterization Factors

Researchers have developed methods to fill inventory data gaps in chemical production systems using basic knowledge of chemical processes and proxy data based on molecular structure. One method was designed specifically to rely on information obtainable from the open literature combined with knowledge of only a few key process characteristics and a set of default estimates for all parameters [20]. A generic input–output process step was used to develop a set of equations to define a mass balance of reactants and products. Onsite production data and pilot scale data from a facility in Switzerland were used to develop default estimates for any missing parameters. Another approach developed by GlaxoSmithKline built a chemical tree of all the process materials used in production of an active pharmaceutical ingredient combined with heuristics to build gate-to-gate inventories [21]. Yet another group evaluated mass and energy flows on the petrochemical production of 338 chemicals to develop models that could estimate key production parameters based on molecular structure [22]. 10 descriptors, including molecular weight, number of functional groups, number of aromatic or aliphatic rings, and others were used to predict cumulative e demand (CED), the global warming potential (GWP), and the Eco-indicator 99 [23]. A tiered approach using extrapolations from existing data, substitution with generic datasets, molecular structure models, and process- based estimation methods were recommended to fill inventory gaps [10].

The life cycle inventory can then be translated to impacts using a variety of impact assessment methods, and the various methods can yield a wide range of results using differing characterization factors for a variety of toxicity endpoints. Wide variation of characterization factors for the same chemicals determined by these various impact assessment methods were recognized as a key challenge for application of LCA to the study of chemical systems. Under the Life Cycle Initiative of the United Nations Environment Programme and the Society of Environmental Toxicology and Chemistry (UNEP/SETAC LCI), a workgroup was formed to develop a consensus model for the impact assessment of chemicals [24]. Seven different models were used to determine characterization factors for a set of 45 chemicals chosen to cover a wide range of property combinations, including environmental partitioning, exposure pathways, overall persistence, long-range transport in air, and the importance of feedback between environmental media [25]. The comparison was used to identify the most important parameters and reasons for differing results. These results were then used to build a new multimedia, multipathway model that links emissions to impacts through environmental fate factors (FF), exposure factors (XF), and effects factors (EF) to calculate characterization factors for human toxicity and freshwater ecotoxicity. Human toxicity factors are expressed as number of cases per kg of chemical emitted, and ecotoxicity factors as potential affected fraction of species in a volume of environmental media per kg of chemical emitted. USEtox models urban air, rural air, agricultural soil, industrial soil, freshwater, and coastal marine water environmental compartments at a continental scale and all but urban air at the global scale. The general framework of the model is shown in Figure 1.1, and additional detail is available from a public web page to disseminate and continually improve the model (USEtox.org).

1.2.2
Linking LCA and Chemical Risk

While the USEtox dramatically reduced the intermodal variation of characterization factors from an initial range of up to 13 orders of magnitude down to no more than two orders of magnitude, this still represents a large band of uncertainty for impact assessment [25]. There are fundamental limitations in applying LCA to assess the chemical risk of alternative chemicals. Although the calculation procedures are similar – estimate emissions, model chemical fate and distribution in various environmental media or compartments, determine concentrations and effects, the calculations are used for different purposes [26]. LCIA aggregates best

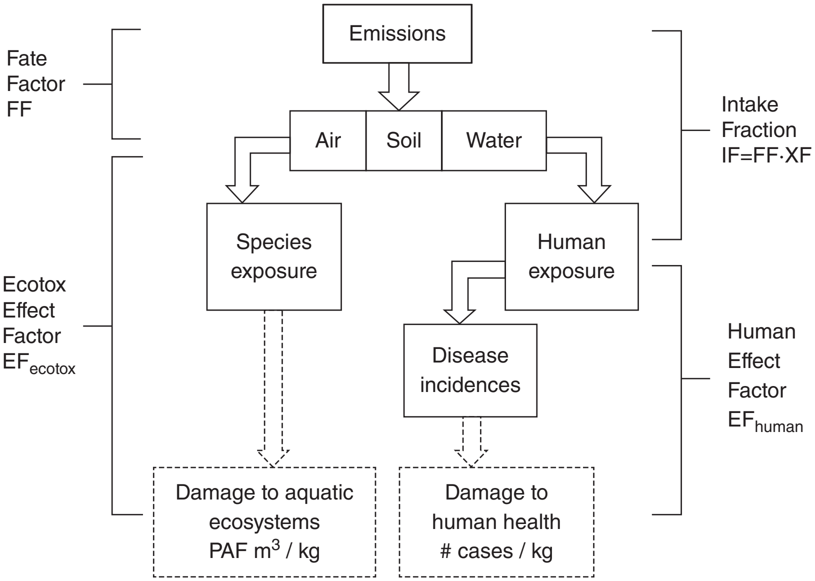

Figure 1.1 Modeling framework for USEtox.

estimates of emissions over time and space to provide a reasonable comparison of alternatives. Midpoint characterization methods link LCI emissions data to an intermediate point in the causal pathway and expresses all emissions in terms of an equivalent unit or emission, such as 1,4-dichlorobenzene equivalents. Endpoint oriented LCIA methods model the cause–effect chain up to the potential damages to human health, ecosystem health, and resources to translate LCI data to quantitative indicators of damage, such as disability adjusted life years (DALYs). Chemical risk assessment uses worst-case assumptions to develop recommendations for risk mitigation methods intended to reduce exposures to a level that results in no observable effects [26]. Thus, risk assessment and LCA answer different questions, and using them in a complementary manner may be more productive than intensive effort to improve the precision of LCA toxicity impact assessments. Even with the current level of uncertainty in toxicity characterization factors, LCIA is adequate to ". . . identify 10–30 chemicals to look at in priority and perhaps, more importantly, to disregard 400 other substances whose impacts are not significant for the considered application (25], p. 544)."

Kuczenski *et al.* [13] have argued LCA could be made more "toxics aware" by explicit modeling of the intermediate flows between unit processes in the system model. Normally, in LCA the intermediate flows are balanced out to yield only the elemental flows to and from nature (i.e., those flows crossing the system boundary) that are used in the impact assessment methods. If toxicity information were attached to the intermediate flows, LCA practitioners could then establish a relationship between the use of a toxic chemical and the function of a product system. The real value for LCA may be in developing a better understanding of the flow of toxics through the product system. In fact, studies have shown that a facility focus on evaluating green chemistry can give misleading results due to outsourcing of process complexity and toxicity to upstream processes, and that a life cycle perspective is critical [27]. One attempt to integrate toxicity information into LCA process models used the risk phrases (R-phrases) as defined in Annex III of European Union Directive 67/548/EEC [28]. A screening tool was developed using SimaPro LCA software. R-phrases were entered for all substances that exceeded concentration limits based on legal requirements for substance and product classification and labeling. The tool did not calculate a score, but simply compiled the data into two lists. An exposure pathway indicator provided information on the most important pathways that in turn identified the recommended risk management measures. A hazard indicator provided information about the need for hazard labeling. Another study characterized wastewater toxicity caused by detergents using data made available through REACH [29].

There are relatively few LCA studies focused strictly on toxicity factors given the limitations already mentioned. It has been used much more frequently to develop a more holistic assessment of a process and to evaluate potential tradeoffs of alternative assessments. For example, solvent use is a significant contributor to the environmental impacts for chemical processes. A variety of studies have developed guidance for solvent selection based on LCA, often evaluating cumulative energy demand, global warming potential and other impacts, as well as toxicity impacts [30,31]. Use of LCA to determine the overall greenness of a process is discussed in the next section.

1.3
Design Material and Energy-Efficient Processes

1.3.1
Introduction

Increasing environmental awareness has pressured companies to become more proactive in addressing public concerns that have expanded beyond production facilities to include all environmental effects of products during use and disposal. Corporate environmental programs have evolved from reactionary and compliance-focused efforts on end-of-pipe controls to limit environmental effects of their production facilities to forward- looking strategies to design inherently safe and green products and processes. However, the definition of what is inherently green is controversial and depends on stakeholder values and priorities and can vary across different product sectors. It is a long and complex procedure that needs a variety of analytical methods and must take into account all the life cycle considerations [32,33].

The mere application of GC principles is not sufficient to achieve a benign design. The design optimization procedure is driven by the application of the fundamental principles, but must consider the entire life cycle of a product [34]. The application of the LCA methodology is recommended as a support and screening tool to identify and quantify opportunities to reduce the environmental impact of products and processes during the design conception process. The value of LCA and life cycle thinking can be attributed to two core aspects – consideration of a broader technical system and a more comprehensive range of environmental impacts. However, both aspects create additional information and computational challenges that can conflict with goals of applying LCA in early design stages.

1.3.2

System Boundaries and Design Guidance

Consideration of the full life cycle is critical to avoid alternatives that impose unintended consequences or simply shift problems to a different place or time. Dichlorodifluoromethane or Freon-12 was originally introduced as a breakthrough safety innovation for refrigerant applications, long before its ozone damaging effects were recognized and made manifest by use as a propellant for aerosols [35]. It is much more cost effective to avoid problems by their identification early in the design than to remediate problems after a product has been put on the market. It has also been argued that aggregating life cycle inventory data across the full product system is necessary to develop a better understanding of the potential impacts of current global supply chains [36]. However, there is limited guidance available for defining appropriate system boundaries, and depending on the goal of the study, impacts can have different boundaries [37]. Further, the design process addresses both the product and the associated manufacturing processes for that product. The product and associated processes each have distinct life cycles imposing specific considerations for LCA [38]. The demands of a holistic life cycle perspective must be balanced against the constraint of limited information and time to integrate life cycle considerations in early design phases.

Zheng *et al.* [39] developed a framework for incorporating sustainability into the conceptual design stage for chemical process development using a waste reduction algorithm. The algorithm was based on the mass and energy balance, and evaluated eight impact categories dependent on chemical properties to assess human and ecological toxicity, and atmospheric impacts for ozone depletion, global warming, acidification, and photochemical oxidation. Other researchers have attempted to use results from early laboratory experiments or pilot scale studies to project the potential impacts of full-scale production systems. Earhart *et al.* [40] translated data from laboratory experiments in terms of environmental impacts in order to verify the feasibility behind the use of the new starting raw material (e.g., the use of fructose to produce polyethylene furandicarboxylate-PEF). However, a review of life cycle process design concluded that advanced process development activities, such as pilot scale facilities did not yield the type and quality of data required for LCA, and recommended enhanced collaboration between researchers and process engineers to improve data availability [41].

Another approach to simplify application of LCA in early process development has been to focus on a specific problem, and use detailed LCA studies to develop recommendations for improved design. For example, the chemical industry uses a wide range of organic solvents having properties of volatility, persistence, and toxicity that make them a priority for environmental assessments [30]. Capello *et al.* [31] developed a framework for assessing solvents using a simplified environmental, health and safety (EHS) screening combined with LCA. The EHS screening included a qualitative measure based on nine hazard categories: release potential, fire/explosion safety, reaction/decomposition safety, acute toxicity, irritation toxicity, chronic toxicity, persistency, air pollution, and water pollution. LCA studies were based on the combined LCIs for the petrochemical production of 45 organic solvents. The framework was then demonstrated on 26 pure organic solvents and several alcohol–water mixtures. Amelio *et al.* [30] expanded on their work to develop guidelines applicable in the early stages of process design that would enable the choice of solvent and the best treatment method (incineration or distillation), based on the composition of the chemical solvent. Their results demonstrated the importance of a full life-cycle perspective. The decision to select incineration or distillation was dependent on the environmental impact originating from the production of the solvents.

Normalization and Weighting

LCIA results can be normalized and weighted to yield a single score metric of the overall impact or greenness. These are optional elements of LCIA to calculate the magnitude of category indicator results relative to a specified reference value (normalization), and to convert and possibly aggregate indicator results across impact categories using quantitative factors based on importance (weighting) [42]. Normalization and weighting are inherently subjective, reflecting the values and priorities of the stakeholder sponsoring or conducting the study. For that reason, these are optional elements. Criteria used for normalization and weighting should be transparent, and the underlying data should be available so that other stakeholders can make independent assessments based on their values and priorities

Yet another approach to address data limitations is to develop qualitative or semi quantitative approaches to streamline the LCA. BASF developed an eco-efficiency tool that characterized chemical products for material and energy consumption, emissions, toxicity potential, and risk potential [43]. Streamlined methods were developed for the various impact categories and transparent methods to normalize and weight the data, allowing results to be displayed in simple “spider charts” (a type of two-dimensional chart that allows display of three or more quantitative variables plotted on axes starting from the same origin). Thus, the tool was effective for informing design as well as communicating results to customers and other stakeholders. The tool was further enhanced to the SEEbalance® instrument [44] that combined the eco-efficiency analysis principle with a social LCA perspective [45]. The eco-efficiency analysis was expanded to include land use impacts, and social impacts were assessed for employees, business partners, end users/consumers, the international community, society, and future generations. Results were displayed in separate charts for eco-efficiency and socio-efficiency, or combined into a three-dimensional cube for graphical displays easy to communicate to different audiences. SEEbalance® represents a successful example of how the whole life cycle perspective can be applied to the management routines in order to improve product performance and capture market advantage with effective communications.

Chimex, a subsidiary of L'Oréal, launched the Eco-footprint tool in 2014 to support a corporate initiative named Made in Chimex™ that was aimed at making social responsibility central to business strategy [46]. The tool rated 10 factors grouped under ecodesign and manufacturing on a scale of 1–4. A variety of streamlined metrics and qualitative measures were defined for each impact category. The tool provided effective guidance for design and presented results in an easy to communicate format.

GlaxoSmithKline (GSK) conducted a detailed assessment of the cradle-to-gate life cycle environmental impacts associated with the manufacturing of materials used in a typical pharmaceutical process to develop a streamlined tool for the Fast LCA of Synthetic Chemistry, FLASC™ [47]. Inventory data were generated for some 140 chemicals and were collated for eight impact categories. Statistical analysis then grouped the chemicals into 14 material classes that allowed generation of average life cycle impact profile data that could be used for materials missing LCI data. The FLASC™ evaluations were later combined with a health score to develop guides ranking commonly used reagents for 15 transformations designed to reduce the environmental impact of drug discovery and development [48].

1.3.3
Impact Categories and Green Metrics

It has been noted that the evolution of LCA in pharmaceutical and chemical applications has been to reduce the level of detail and extend the system boundary [37]. There has also been a push to develop simple green metrics to simplify integration of life cycle insights into routine decision-making processes [49,50]. Thus, there is a continual tension between abbreviated approaches to push greater integration of life cycle approaches and more holistic assessments to avoid burden shifting and/or unintended consequences. The examples already discussed highlight that different sectors and different classes of products have different priorities and hence methods need to be tailored to the specific context. It has further been stressed that system boundaries and other details of the study should be defined with the goal and scope of the study in mind. In many cases, simple green metrics are valid and practical, but should be supported with strategic use of LCA to define the limitations of their use.

Simplified green metrics are grounded in the observation that qualitative assessments or studies involving a limited set of impact categories are sufficient in many cases to identify the key drivers of environmental impact. For example, in a study of catalytic methods to avoid phosphine oxide waste products in phosphorous-consuming pathways, cumulative energy demand was used as a proxy for total environmental burden in combination with greenhouse gas emissions [51]. One study evaluated various green metrics – reactant stoichiometry, yield, atom economy, carbon efficiency, reaction mass efficiency, mass intensity (excluding water), and mass productivity for a series of reactions [49]. The study concluded that while some of the metrics were useful as organizing concepts or for communicating with business managers, none captured the range of issues necessary to ensure sustainable solutions. The pharmaceutical industry, through the American Chemical Society Green Chemistry Institute Pharmaceutical Roundtable selected process mass intensity (PMI) as the key mass-based green metric [50]. PMI is defined as the total mass of materials used to produce a specified mass of product and is given by Eq. (1.1).

$$\text{PMI} = \frac{\text{total mass in a process or process step(kg)}}{\text{mass of product(kg)}} \tag{1.1}$$

Choice of the PMI metric was argued as necessary to truly integrate green chemistry and engineering into chemical processes: Considering inputs, PMI is a leading metric to facilitate changes as the processes and synthesis routes are being designed and tested. It was contrasted with *E*-factor, a metric that focuses on waste generated per unit of product, as shown in Eq. (1.2).

$$E\text{-factor} = \frac{\text{total mass of waste(kg)}}{\text{mass of product(kg)}} \tag{1.2}$$

E-factor was considered to be a legacy of end-of-pipe waste management approaches of the 1980s. The philosophical difference of these metrics reflects a broader discussion of LCIA methods and sustainability objectives. LCIA and sustainability are concerned with evaluating potential constraints imposed on human industrial systems by the natural environment. These constraints can be due to resource depletion (limits of nature to provide basic materials and fuels used by the economy) or due to damages to human and/or ecosystem health (limits of nature on absorbing wastes thrown off by the economy). It is important to take a life cycle perspective that considers the effects of both inputs and outputs.

There is a tension between simple metrics or abridged LCA methods intended to promote use in business decision making processes and preserving the value of a comprehensive LCA. There are, however, inherent limitations to LCA methods yielding precise assessments of the greenness of production systems. LCA models assume static conditions, and thus will always need to be used in conjunction with more detailed process modeling to evaluate optimum operating conditions and to assess dynamic effects. In addition, even the simplest LCA could have hundreds of inventory items, making interpretation of the results extremely difficult. Classifying inventory results into a handful of impact categories greatly aids the interpretation of results and facilitates identification of trade-offs, but even interpreting and communicating LCIA results can be challenging and numerous formats have been suggested to aid the process [52]. The real value of LCA is providing a better understanding of the broader system within which the specific problem or project is encapsulated, identifying and quantifying key trade-offs, promoting improved communication and collaboration across functional units within the company and external stakeholders, and developing insights about actionable changes to improve the product or process [37,38,41].

1.3.4
Policy Implications

The studies already discussed typically invoke an assumption of *ceteris paribus*, or all other things being equal. Even though the studies promoted a broader consideration of the full product system life cycle, the scope was focused on improvement actions of a specific company or organization and did not take into account broader market changes that might occur, such as substitution effects, economies of scale, and elasticity of supply and demand [53]. Thus, when considering broader sustainability initiatives or public policy reform, researchers have argued for a consequential LCA (C-LCA) that models the indirect changes induced by the proposed initiative [54,55]. The more common accounting or attributional LCA (A-LCA) uses average data to make relative assessments of environmental performance, while C-LCA uses marginal data and broader system boundaries that include indirectly impacted processes to assess ". . . how flows to and from the environment will change as a result of different potential decisions (54], p. 856)." A number of approaches have been proposed for integration of economic modeling with LCA to account for these broader market shifts [53,56].

Plevin *et al.* [57] argued that use of A-LCA to estimate climate change mitigation benefits can mislead policy makers. Deciding when and how to apply C-LCA versus A-LCA is an ongoing debate. What is clear, however, is that decisions will be more resilient if based on assessment of a wider range of plausible scenarios [57]. But the critical question remains – how does one decide which technologies or processes might be affected by the decision under consideration? Weidema *et al.* [58] proposed a series of questions to help identify affected technologies and provided examples of how the questions can be applied across various sectors.

1) What time horizon does the study apply to?
2) Does the change only affect specific processes or a market?
3) What is the trend in the volume of the affected market?

4) Is there potential to provide an increase or reduction in production capacity?
5) Is the technology the most/least preferred?

For example, the ban or lead solder to reduce toxic emissions of lead to landfills was expected to result in broad shifts, raising important questions about what happens to the lead no longer used in solder, as well as questions concerning trade-offs attributable to the higher reflow temperatures for lead-free alternatives [59]. These broader issues are particularly relevant for policies to promote a shift to renewable feedstocks, discussed in the following section. It is obvious that integrating necessary economic and social science disciplines to combine GC principles within a C-LCA perspective during early design stages is a difficult task that remains very much a work in progress.

1.4
Promote Renewable Materials and Energy

1.4.1
Introduction

The use of renewable feedstocks is one of the 12 principles of green chemistry [1], and increasing the use of biomass for the production of fuels, energy, and chemicals is seen by many as an important strategy toward sustainable development [60]. In 2012, the United States and Europe communicated their intentions to grow their bio economies [61,62]. In addition, many other countries now have bioeconomy strategies in place [63]. Globally, bioenergy is expected to contribute about one-quarter (138 EJ) of primary energy demand based on various renewable energy scenarios [64]. The share of biochemicals is foreseen to increase globally from about 3–4% in 2010 to 7–17% in 2025 [65].

Much of the strong support for the use of biomass feedstock to substitute oil derivatives is premised on the widespread assumption that they are carbon neutral, promote rural development, and provide an opportunity for countries to decrease dependence on imported oil. However, biomass production also takes up land and may compete with food production, and there is no consensus among scientists on how to evaluate biomass sustainability [63]. Even though the current ISO standards [3,42] provide a general framework for conducting LCAs, they fail to address a number of critical issues associated with bio-based products (i.e., chemicals, materials, energy) from a life cycle wide perspective. These issues include, for example, the accounting for bio-based carbon storage, impacts of land use changes, and consequential impacts of biomass diversion [66].

1.4.1.1 Glycerol Case Study

Glycerol presents an interesting case study of the challenges of analyzing the impacts of policies to promote renewables. Biodiesel is generally produced by a transesterification reaction between triglycerides and methanol, and glycerol is a

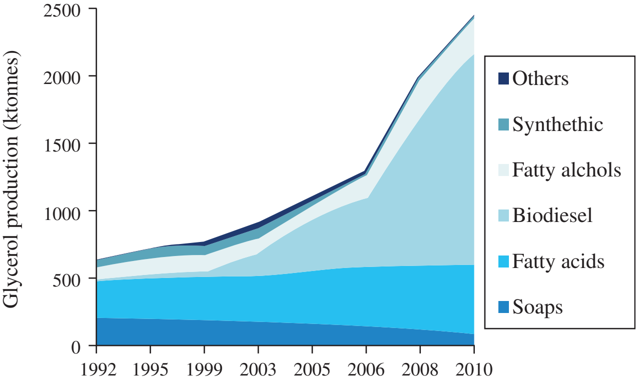

Figure 1.2 Glycerol worldwide production per year, compilation based on Ref. [68].

by-product. The booming market for biodiesel fuels driven by government programs to promote renewable fuels for transportation has created a surplus of glycerol (see Figure 1.2). Countries with large areas of available land, such as Argentina and Brazil, and countries with established palm or coconut oil plantations, such as Malaysia, Thailand, the Philippines, Indonesia, and Columbia, expanded production to sell to biodiesel producers in Europe and North America and oleochemical producers in Asia [67]. Thus, supply of glycerol is independent of the demand, and the surplus has created interest in developing new chemical uses of glycerol as a platform chemical.

Morales *et al.* [69] studied the synthesis of lactic acid in a process building on the enzymatic production of dihydroxyacetone from crude glycerol. Their LCA study used ecoinvent datasets [70] and Aspen Plus® V8.2 process models to estimate relevant inventory data. Nonrenewable cumulative energy demand was used as a proxy for environmental impact. The ecoinvent data were based on rapeseed oil grown in Europe. Allocation of impacts assumed that glycerol was a partially utilized coproduct, and is valid as long as the supply of glycerol is not constrained by reductions in biodiesel production. Thus, policies to promote sustainable transport fuels directly impacted assessment of biochemicals produced from glycerol.

Cespi *et al.* [71] studied the production of acrolein using glycerol as a feedstock. Acrolein is an important intermediate in industrial (acrylic acid – AcA) and agricultural (methionine) chemicals. Two synthesis routes producing glycerol as a by-product were modeled – transesterification process for biodiesel and production of fatty acids by triglyceride hydrolysis – and compared using a life cycle perspective with the traditional fossil-based pathway involving the partial oxidation of propylene.

In general, the integration of the life cycle approach within the R&D stage helps to better understand production chain criticalities and to optimize the whole manufacturing process. Given the case of the AcA, the application of a simplified cradle-to-gate assessment using contribution and network analyses

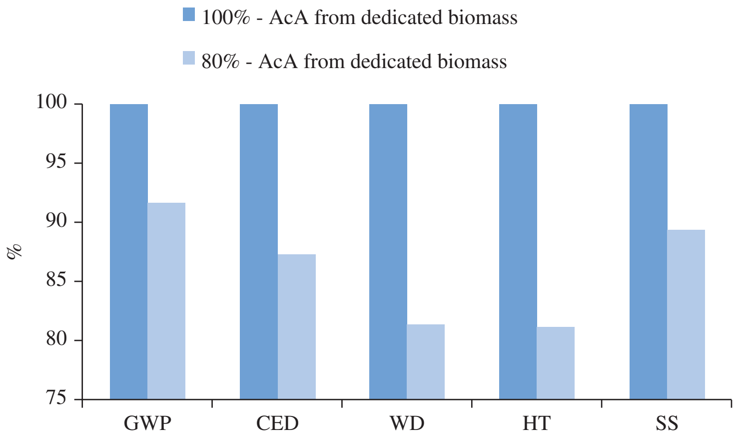

Figure 1.3 Reduction of impacts with substitution of 20% WCO.

underlines the stages with higher environmental concerns and can help enterprises to implement their monitoring plan to find more affordable solutions. Assuming a basic scenario in which glycerol is obtained from dedicated biomass only (e.g., rapeseed), the execution of a network analysis depicted the process responsible for the greater environmental burdens expressed in terms of the main indicators, such as: climate change (GWP), cumulative energy demand, water depletion (WD), human toxicity (HT) and single score (SS). In this case, the crop production phase is the major contributor for each impact category considered (around 50–86%). Therefore, improvement efforts would be best focused on alternatives for the raw material supply. One option could be the substitution of dedicated plant feedstock with recovery of a waste product, such as waste cooking oil (WCO). As depicted in Figure 1.3, a replacement of only 20% of the virgin oil with the WCO could yield potential reduction of the impact categories considered on the order of 8–19%.[2]

In addition to the environmental concerns, a broader interpretation of greenness to encompass sustainability objectives would expand the analysis to include some social evaluation such as the potential impacts on humanity. HT indicator should be always taken into consideration in product/process assessments. The SS indicator incorporates weighting of the various impact categories. Different stakeholders would have different values and priorities, and the weighting can be adjusted to accommodate differing perspectives. Substitution of WCO could create a revenue stream for restaurants and other institutional kitchens that generate the waste. The substitution would also impact the revenue of farms and plantations currently providing the plant oils. Further, the actual GHG

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2) The authors acknowledge Professors Dr. Fabrizio Passarini and Dr. Fabrizio Cavani from the University of Bologna for the use of the software license and the sensible data to run the analysis.

reductions achieved depend on fossil fuel market responses to substitution of biodiesel. Thus, the quantitative LCA results are necessarily supplemented with qualitative assessments of potential market responses, social impacts, and other political and technology trends to define scenarios that can test the robustness of proposed alternatives [37,38]. It is also particularly important for broad public policy initiatives to promote renewables to take a consequential perspective in LCA studies. Another area of special consideration is geographic specificity. Many land use, water pollution, and toxicity issues are localized. On the other hand, when commodity production is under investigation (e.g., butadiene) it is appropriate to focus on global concerns, for example, GWP, WD, and CED [72]. Thus, studies to evaluate the ultimate benefits of renewable feedstocks present numerous methodological challenges.

1.4.2
Biochemicals Production

1.4.2.1 Life Cycle Stages of Biochemical Production

The environmental impacts of bio-based chemicals and materials have been quantified using LCA in numerous studies (see, e.g., [73–79). Figure 1.4 shows a simplified and generic system boundary for a biorefinery system [80,81] producing chemicals, fuel, and energy from bio-based feedstocks (biomass or organic waste feedstock).

A typical life cycle starts with carbon fixation from the atmosphere via photosynthesis in the biomass crop. Renewable feedstock can be obtained from various sectors, including agriculture, forestry, aquaculture, industries (process residues, construction, and demolition debris), and households (municipal wastes and wastewater). Land requirements vary with feedstock type [82]. A conceptual biorefinery is capable of supplying a wide spectrum of marketable products, including chemicals, fuels, and bioenergy [83]. In addition to biochemical conversion routes (i.e., fermentation or anaerobic digestion), thermochemical platforms apply gasification or pyrolysis as a way of transforming bio-based feedstock into fuels, energy, and chemical products [84]. Biopolymers (e.g., polyethylene or polylactic acid) may be used in a cascading manner (multiple life cycles), thereby delaying emissions of carbon stored in the polymer product to the environment [76,85]. However, most of today's biochemicals are produced in single production chains and not yet within a biorefinery setting [86].

1.4.2.2 Environmental Implications of Biomass Production

Several scientific studies have shown the potential of bio-based fuels, energy, chemicals, and materials to reduce both nonrenewable energy consumption and carbon dioxide emissions in comparison to their fossil-based counterparts [79]. However, biomass production and processing is also associated with adverse environmental impacts. For example, agricultural biomass production can have

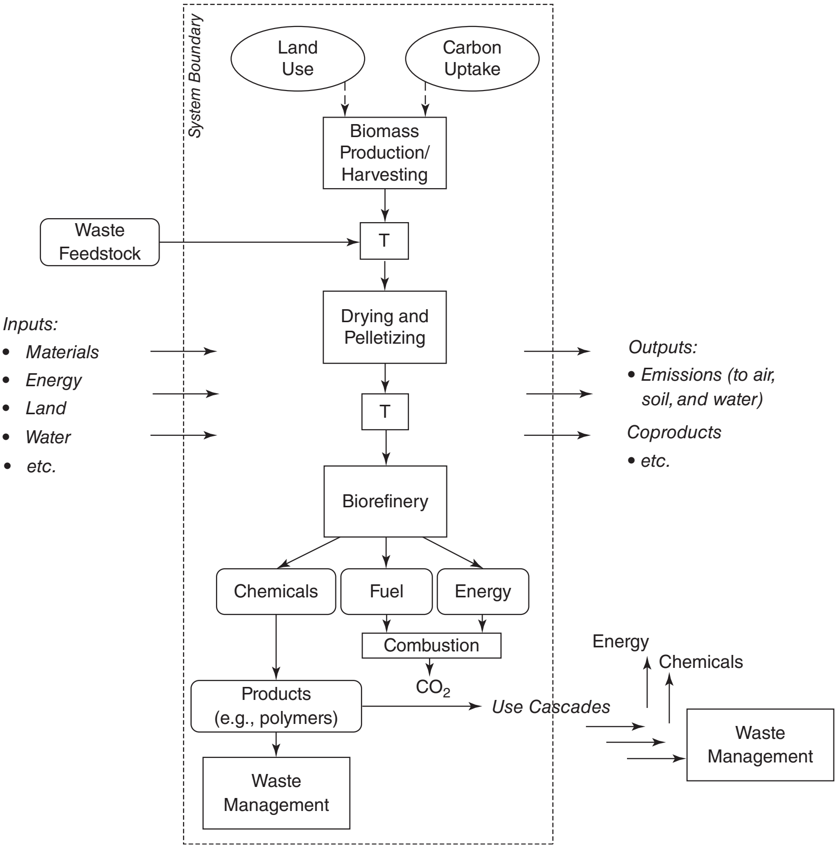

Figure 1.4 Schematic production chain of biochemical production in a biorefinery concept (biochemical platform).

negative environmental effects such as soil erosion, eutrophication of ground and surface waters, and destruction of ecosystems resulting in diminished biodiversity [87]. Cultivation, harvesting, and subsequent processing of biomass feedstock consumes fossil energy and requires the energy intensive production and use of artificial fertilizers and hazardous chemicals. Environmental impacts from eutrophication and acidification as well as N_2O emissions, which is a particularly strong greenhouse gas, are often times not properly accounted for in LCA studies on bioproducts [87]. Furthermore, the use of phosphorus as plant fertilizer is gaining increasing attention as a "critical" (and nonsubstitutable) raw material upon which crop growth depends [88].

LCI data to support impacts to eutrophication or acidification during biomass production are often scarce. Biodiversity and other ecosystem impacts are highly site specific and difficult to quantify, given current LCIA methods [89,90]. Assessment methods for water use, soil degradation, and biodiversity are immature and need further development [66]. So far, none of the LCIA methods consider aspects of criticality [91] associated with using phosphorus and minerals for fertilization.

1.4.2.3 Carbon Accounting and Land Use Change

In recent years, the carbon neutrality presumption of biomass feedstock in LCA has been challenged as indirect emissions of land use change [92,93], the dynamics of carbon flow over time [94,95], and temporary carbon storage in products [96] are receiving increased attention (see Figure 1.5).

Until recently, many LCA studies presumed that biomass is inherently carbon neutral because it is part of the natural carbon cycle [97]. However, in a seminal paper, researchers challenged the greenhouse gas balance of bioethanol production in the United States, and suggested indirect links between diverting cropland for biofuels production and conversion of forest and grassland to new cropland to replace the grain diverted to biofuels [92]. Greenhouse gas emissions can occur as land is converted from one use to another (e.g., forest land to cropland) because of differences in the amount of carbon stored in the plants and potential losses of soil carbon (termed: "direct land use change") [98]. However, "indirect land use changes" occur outside the system boundary (Figure 1.5) and are due to the displacement of services (usually food production) that were previously provided by the land now used for growing crops for the production of bioproducts [92,93,98]. LCA researchers attempt to capture such indirect impacts using consequential LCA [53] but there is no general consensus yet on how to do such assessments, and coupling LCA models with econometric

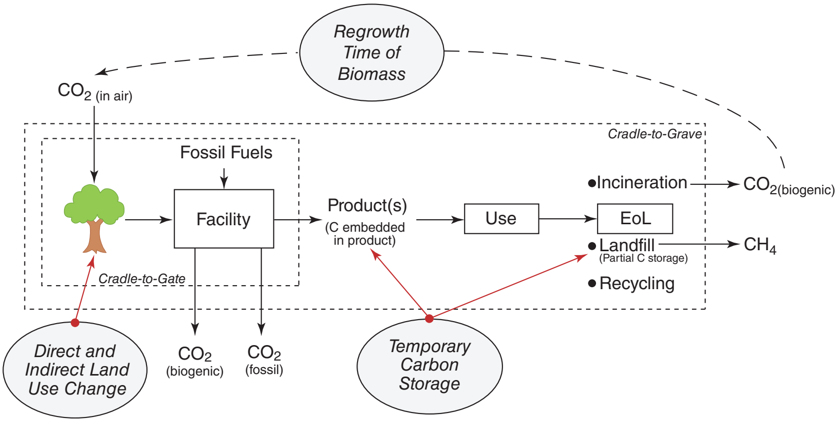

Figure 1.5 Schematic figure showing the three areas of debate in calculating the greenhouse gas emissions of bio-based products: (1) direct and indirect emissions of land use change, (2) regrowth time of biomass, and (3) temporary carbon storage.

models (accounting for changes in supply and demand of feedstock diversion) is challenging. Greenhouse gas emissions from indirect land use change will depend on the type of lands converted and what other product system (e.g., food production) compete with the growth of biomass feedstocks.

Once land use changes have been identified and inventoried, there remains a difficult task to quantify the impacts. Land use interventions are characterized as occupational or transformational, and land quality is assessed for impacts on the intrinsic value of biodiversity, on the biotic production potential, and on ecological soil quality [99]. Although assessment methods are under development, UNEP–SETAC has issued guidance for global land use impacts on biodiversity and ecosystem services [100].

Temporary carbon storage can take place if carbon sequestered via photosynthesis from the atmosphere is stored in a bio-based product (e.g., polymer with long life time) [96]. Carbon storage can also occur at end-of-life (EoL), for example, when a bio-based product is landfilled [101,102]. Some studies have suggested that temporary carbon storage delays radiative forcing from greenhouse gases in the atmosphere and that delay provides time for technological progress and research [96] and should therefore, be accounted for. Other studies argue that biogenic carbon storage should not be considered because it is usually reversible, and therefore, inevitably adds carbon back into the atmosphere in the future. Another consideration is that delayed emissions could occur in an atmosphere with a higher CO_2 concentration, producing even greater impacts [103]. The benefits of biogenic carbon storage depend on the time horizon over which the global warming potential of greenhouse gas emissions is considered [66]. A time window of 100 years (beyond which the impacts of carbon storage are not considered) is often used, although it should be noted that the choice is intrinsically subjective [96].

The majority of current LCA models ignore the time required for the harvested biomass to regrow and sequester the biogenic carbon released during the life cycle of the bio-based product [98]. While this assumption is a reasonable approximation for short rotation crops (requiring about one year for regrowth), it neglects the fact that many feedstocks (e.g., forest biomass) will need more time to regrow and sequester an equal amount of carbon as was released during the bioproduct's life cycle. Ideally, this time component would be included by coupling LCA models with forest carbon models [94,95], but in reality this is rarely done.

Multiple approaches accounting for biogenic carbon in LCAs of bio-based products exist. Simply ignoring biogenic carbon emissions has a high potential of burden shifting as many of the impacts may be located outside the general LCA system boundary (e.g., indirect land use change due to feedstock diversion may take place in other geographical regions; sequestration of biogenic carbon emitted during the production of bio-based products in new biomass feedstock may require multiple years and be outside the temporal scope of the LCA).

1.4.2.4 Global Availability of Arable Land

In view of current efforts to increase commercial biofuels and biochemicals production, the availability of global arable land for nonfood purposes requires special attention. Reference [104] showed that *global cropland area*, which encompasses arable land and permanent crops, *is in fact a scarce resource*. Their study estimated that global demand for cropland area will increase mainly due to global population growth and changes in nutrition. As a result, cropland availability per capita will decrease from 2500 m^2 per person in 2004 to only about 2000 m^2 per person in 2030. This does not yet consider the increasing land required for providing future demands for bio-based fuels, chemical, and energy. Furthermore, climate change may lead to a higher frequency of extreme weather patterns.

Considering land occupation of bio-based products together with other impact categories is important because land is a scarce resource. The pressure on global arable land can be reduced, for example, by considering the use of waste and production residues instead of virgin biomass as starting materials for green chemistry routes and by producing materials first that can be used in subsequent product life cycles (e.g., polymers produced into plastics that then serve as feedstock for subsequent chemicals or energy production) [82,87].

1.5

Conclusion and Recommendations

LCA can help to incorporate a more holistic cradle-to-grave and system- wide perspective into GC applications. It can assist in measuring the overall greenness of the 12 principles of green chemistry applied to modern product system and elucidate potential trade-offs (e.g., shifting of environmental burdens from one life cycle stage to another or from one environmental threat to another). However, LCA is not a substitute for chemical risk assessment or more detailed process system engineering studies. The potential value of LCA is in using it complementary to other analytical methods to obtain a more complete picture of the product system and to better target the detailed supporting studies.

There are some inherent limitations in applying LCA to study the multitude of chemical substances used by the modern chemical industry. Missing LCI data are often mentioned as a barrier, but researchers have identified promising approaches to address this need. The use of proxy data with default values based on industry or company-specific data can provide reasonable estimates. Companies can also conduct detailed studies of existing products to develop proxies based on classes of systems with similar impacts. This suggests that there needs to be as much attention on the architecture of data sets as on the specific LCI data elements. The first LCA study will obviously be challenging, and companies should start with simple qualitative assessments. Retrospective studies of deployed products can help develop proxy data sets as already discussed. Improved collaboration across functional groups is important to minimize the administrative burden of gathering data and better coordinate data transfer between R&D, process engineering, product design, and environmental management. Because LCA examines inputs (resources) and outputs (emissions, wastes, and desired products) across the entire product life cycle, from resource extraction to ultimate disposal, its models are usually not site-specific that poses challenges when quantifying toxicity-related impacts and other regional environmental implications. LCA, however, can provide a useful screen for product systems with a global supply chain to identify the 10–30 chemicals that warrant more detailed risk assessment.

Another challenge for LCA is that intermediate flows are balanced out to identify only the elemental flows directly to and from nature, that is, resources used and pollutants emitted. Making the LCI model "toxic aware" could provide useful information to better associate risks with specific processes. The use of risk or R- phrases to integrate toxicity information into LCI models is an interesting approach worth further development. This could provide a valuable interconnection to environmental management programs by helping to identify necessary risk management measures and hazard labeling requirements.

Perhaps the most significant advantage of LCA is providing a structured framework to better integrate GC objectives into product and process design procedures. Simple green metrics or abridged LCA screening methods that are tailored to specific sectors or company objectives can be developed to promote their use in decision-making processes. These simplified approaches can be calibrated with retrospective studies of fielded products or implemented processes. Data collected to manage the operations can then be used to build proxy data sets to speed subsequent LCI efforts. This enables LCA to be used during the early design phase of new green chemistry routes in a streamlined fashion to obtain a first impression of the potential environmental implications of using different process designs and raw materials. Applied strategically, LCA can promote more effective collaboration (and information sharing) across functional groups and supply chain partners and guide organizational learning to continually improve the life cycle performance of the value chain.

Recent efforts of LCA have focused on capturing indirect effects in product supply chains and across the economy through the use of economic models and techniques. The broader consideration of indirect environmental burdens is particularly important for evaluating policies to promote a transition to bio-based raw materials in chemical synthesis. This is an area in need of additional research to develop a better understanding of alternative approaches to C-LCA modeling, improved LCIA methods for land and water use, and more guidance on modeling temporary carbon storage for bio-based chemicals.

References

1 Anastas, P.T. and Warner, J.C. (1998) *Green Chemistry: Theory and Practice*, Oxford University Press, New York.

2 Muñoz, I. (2012) LCA in Green Chemistry: a new subject area and call for papers. *International Journal of Life Cycle Assessment*, **17**, 517–519.

3 ISO14040 (2006) Environmental Management – Life Cycle Assessment – Principles and Framework, Geneva, Switzerland.

4 Finnveden, G., Hauschild, M.Z., Ekvall, T., Guinée, J.B., Heijungs, R., Hellweg, S., Koehler, A., Pennington, D., and Suh, S. (2009) Recent developments in life cycle assessment. *Journal of Environmental Management*, **91**, 1–21.

5 Hellweg, S. and Milà i Canals, L. (2014) Emerging approaches, challenges and opportunities in life cycle assessment. *Science*, **344**, 1109–1113.

6 Reap, J., Roman, F., Duncan, S., and Bras, B. (2008a) A survey of unresolved problems in life cycle assessment: Part 1-goal and scope and inventory analysis. *International Journal of Life Cycle Assessment*, **13**, 290–300.

7 Reap, J., Roman, F., Duncan, S., and Bras, B. (2008b) A survey of unresolved problems in life cycle assessment: Part 2-impact assessment and interpretation. *International Journal of Life Cycle Assessment*, **13**, 374–388.

8 Olsen, S.I., Christensen, F.M., Hauschild, M.Z., Pedersen, F., Larsen, H.F., and Tørsløv, J. (2001) Life cycle impact assessment and risk assessment of chemicals - a methodological comparison. *Environmental Impact Assessment Review*, **21**, 385–404.

9 Tufvesson, L.M., Tufvesson, P., Woodley, J.M., and Börjesson, P. (2013) Life cycle assessment in green chemistry: overview of key parameters and methodological concerns. *International Journal of Life Cycle Assessment*, **18**, 431–444.

10 Wernet, G., Hellweg, S., and Hungerbühler, K. (2012) A tiered approach to estimating inventory data and impacts of chemical products and mixtures. *International Journal of Life Cycle Assessment*, **17**, 720–728.

11 Anastas, P.T. and Lankey, R.L. (2000) Life cycle assessment and green chemistry: the yin and yang of industrial ecology. *Green Chemistry*, **2**, 289–295.

12 Kralisch, D., Ott, D., and Gericke, D. (2015) Rules and benefits of life cycle assessment in green chemical process and synthesis design: a tutorial review. *Green Chemistry*, **17**, 123–145.

13 Kuczenski, B., Geyer, R., and Boughton, B. (2011) Tracking toxicants: toward a life cycle aware risk assessment. *Environmental Science and Technology*, **45**, 45–50.

14 Sjöström, J. (2006) Green chemistry in perspective – models for GC activities and GC policy and knowledge areas. *Green Chemistry*, **8**, 130–137.

15 ICA (2013) Alternatives Assessment Guide, Interstate Chemicals Clearinghouse, pp. 166.

16 Lavoie, E.T., Heine, L.G., Holder, H., Rossi, M.S., Lee, R.E., II, Connor, E.A., Vrabel, M.A., DiFiore, D.M., and Davies, C.L. (2010) Chemical alternatives assessment: enabling substitution to safer chemicals. *Environmental Science and Technology*, **44**, 9244–9249.

17 Rossi, M., Tickner, J., and Geiser, K. (2006) Alternatives Assessment Framework of the Lowell Center for Sustainable Production, pp. 21.

18 Wernet, G., Conradt, S., Isenring, H.P., and Jiménez-González, C. (2010) Life cycle assessment of fine chemical production: a case study of pharmaceutical synthesis. *International Journal of Life Cycle Assessment*, **15**, 294–303.

19 Hellweg, S., Fischer, U., Scheringer, M., and Hungerbühler, K. (2004) Environmental assessment of chemicals: methods and application to a case study of organic solvents. *Green Chemistry*, **6**, 418–427.

20 Geisler, G., Hofstetter, T.B., and Hungerbühler, K. (2004) Production of fine and specialty chemicals: procedure for the estimation of LCIs. *International Journal of Life Cycle Assessment*, **9**, 101–113.

21 Jiménez-González, C., Curzons, A.D., Constable, D.J.C., and Cunningham, V.L. (2004) Cradle- to- gate life cycle inventory and assessment of pharmaceutical compounds. *International Journal of Life Cycle Assessment*, **9**, 114–121.

22 Wernet, G., Papadokonstantakis, S., Hellweg, S., and Hungerbühler, K. (2009)

Bridging data gaps in environmental assessments: modleing impacts of fine and basic chemical production. *Green Chemistry*, **11**, 1826–1831.

23 Goedkoop, P., and Spriensma, R. (2001) *The Eco-Indicator 99: A Damage Oriented Method for Life Cycle Impact Assessment, Methodology Report*, PRé Consultants, Amersfoort, NL.

24 Hauschild, M.Z., Huijbregts, M.A.J., Jolliet, O., MacLeod, M., Margni, M., van de Meent, D., Rosenbaum, R.K., and McKone, T.E. (2008) Building a model based on scientific consensus for life cycle impact assessment of chemicals: the search for harmony and parsimony. *Environmental Science & Technology*, **42**, 7032–7037.

25 Rosenbaum, R.K., Bachmann, T.M., Swirsky Gold, L., Huijbregts, M.A.J., Jolliet, O., Juraske, R., Koehler, A., Larsen, H.F., MacLeod, M., Margni, M. *et al.* (2008) USEtox - the UNEP-SETAC toxicity model: recommended characterization factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. *International Journal of Life Cycle Assessment*, **13**, 532–546.

26 Askham, C. (2012) REACH and LCA – methodological approaches and challenges. *International Journal of Life Cycle Assessment*, **17**, 43–57.

27 Roschangar, F., Sheldon, R.A., and Senanayake, C.H. (2015) Overcoming barriers to green chemistry in the pharmaceutical industry – the Green Aspiration Level™ concept. *Green Chemistry*, **17**, 752–768.

28 Askham, C., Gade, A.L., and Hanssen, O.J. (2013) Linking chemical risk information with life cycle assessment in product development. *Journal of Cleaner Production*, **51**, 196–204.

29 Igos, E., Moeller, R., Benetto, E., Biwer, A., Guiton, M., and Dieumegard, P. (2014) Development of USEtox characterisation factors for dishwasher detergents using data made available under REACH. *Chemosphere*, **100**, 160–166.

30 Amelio, A., Genduso, G., Vreysen, S., Luis, P., and Van der Bruggen, B. (2014) Guidelines based on life cycle assessment for solvent selection during the process design and evaluation of treatment alternatives. *Green Chemistry*, **16**, 3045–3063.

31 Capello, C., Fischer, U., and Hungerbühler, K. (2007) What is a green solvent? A comprehensive framework for the environmental assessment of solvents. *Green Chemistry*, **9**, 927–934.

32 Anastas, P.T. and Zimmerman, J.B. (2003) Peer reviewed: design through the 12 principles of green engineering. *Environmental Science and Technology*, **37**, 94A–101A.

33 Jiménez-González, C. and Constable, D.J.C. (2011) *Green Chemistry and Engineering: A Practical Design Approach*, Wiley-VCH Verlag GmbH, Weinheim, Germany.

34 Gilbertson, L.M., Zimmerman, J.B., Plata, D.L., Hutchison, J.E., and Anastas, P.T. (2015) Designing nanomaterials to maximize performance and minimize undesirable implications guided by the principles of green chemistry, *Chemical Society Reviews*, **44**, pp. 5758–5777.

35 Tenner, E. (1996) *Why Things Bite Back*, Vintage Books, New York.

36 Burgess, A.A. and Brennan, D.J. (2001) Application of life cycle assessment to chemical processes. *Chemical Engineering Science*, **56**, 2589–2604.

37 Jiménez-González, C. and Overcash, M.R. (2014) The evolution of life cycle assessment in pharmaceutical and chemical applications – a perspective. *Green Chemistry*, **16**, 3392–3400.

38 Jacquemin, L., Pontallier, P.-Y., and Sablayrolles, C. (2012) Life cycle assessment (LCA) applied to the process industry: a review. *International Journal of Life Cycle Assessment*, **17**, 1028–1041.

39 Zheng, K., Lou, H.H., Gangadharan, P., and Kanchi, K. (2012) Incorporating sustainability into the conceptual design of chemical process-reaction routes selection. *Industrial & Engineering Chemistry Research*, **51**, 9300–9309.

40 Eerhart, A.J.J.E., Faaij, A.P.C., and Patel, M.K. (2012) Replacing fossil based PET with biobased PEF; process analysis,

energy and GHG balance. *Energy & Environmental Science*, **5**, 6407–6422.

41 Fazeni, K., Lindorfer, J., and Prammer, H. (2014) Methodology advancements in life cycle process design: a preliminary outlook. *Resources, Conservation and Recycling*, **92**, 66–77.

42 ISO 14044 (2006) Environmental Management – Life Cycle Assessment – Requirements and Guidelines, Geneva, Switzerland.

43 Saling, P., Kicherer, A., Dittrich-Krämer, B., Wittlinger, R., Zombik, W., Schmidt, I., Schrott, W., and Schmidt, S. (2002) Eco-efficiency analysis by BASF: the method. *The International Journal of Life Cycle Assessment*, **7**, 203–218.

44 Schmidt, I., Meurer, M., Saling, P., Kicherer, A., Reuter, W., and Gensch, C.-O. (2004) SEEbalance®: managing sustainability of products and processes with the socio- eco- efficiency analysis by BASF. *Greener Management International*, **45**, 79–94.

45 UNEP/SETAC (2009) *Guidelines for Social Life Cycle Assessment of Products* (eds C. Benoit and B. Mazjin), United Nations Environment Programme, Paris.

46 Leseurre, L., Merea, C., Duprat de Paule, S., and Pichart, A. (2014) Eco- footprint: a new tool for "Made in Chimex" considered approach. *Green Chemistry*, **16**, 1139–1148.

47 Curzons, A., Jiménez-González, C., Duncan, A., Constable, D.C., and Cunningham, V. (2007) Fast life cycle assessment of synthetic chemistry (FLASC™) tool. *The International Journal of Life Cycle Assessment*, **12**, 272–280.

48 Adams, J.P., Alder, C.M., Andrews, I., Bullion, A.M., Campbell-Crawford, M., Darcy, M.G., Hayler, J.D., Henderson, R.K., Oare, C.A., Pendrak, I. *et al.* (2013) Development of GSK's reagent guides – embedding sustainability into reagent selection. *Green Chemistry*, **15**, 1542–1549.

49 Constable, D.J.C., Curzons, A.D., and Cunningham, V.L. (2002) Metrics to "green" chemistry – which are the best? *Green Chemistry*, **4**, 521–527.

50 Jimenez-Gonzalez, C., Ponder, C.S., Broxterman, Q.B., and Manley, J.B. (2011) Using the right green yardstick: why process mass intensity is used in the pharmaceutical industry to drive more sustainable processes. *Organic Process Research & Development*, **15**, 912–917.

51 van Keleren, H.A., Blom, A.L., Rutjes, F.P.J.T., and Huijbregts, M.A.J. (2013) On the usefulness of life cycle assessment in early chemical methodology development: the case of organophosphorous-catalyzed Appel and Wittig reactions. *Green Chemistry*, **15**, 1255–1263.

52 Harding, K.G. (2013) A technique for reporting life cycle impact assessment (LCIA) results. *Ecological Indicators*, **34**, 1–6.

53 Earles, J.M. and Halog, A. (2011) Consequential life cycle assessment: a review. *The International Journal of Life Cycle Assessment*, **16**, 445–453.

54 Curran, M.A., Mann, M., and Norris, G. (2005) The international workshop on electricity data for life cycle inventories. *Journal of Cleaner Production*, **13**, 853–862.

55 Weidema, B. (1993) Market aspects in product life cycle inventory methodology. *Journal of Cleaner Production*, **1**, 161–166.

56 Marvuglia, A., Benetto, E., Rege, S., and Jury, C. (2013) Modelling approaches for consequential life-cycle assessment (C-LCA) of bioenergy: critical review and proposed framework for biogas production. *Renewable and Sustainable Energy Reviews*, **25**, 768–781.

57 Plevin, R.J., Delucchi, M.A., and Creutzig, F. (2014) Using attributional life cycle assessment to estimate climate-change mitigation benefits misleads policy makers. *Journal of Industrial Ecology*, **18**, 73–83.

58 Weidema, B., Frees, N., and Nielsen, A.-M. (1999) Marginal production technologies for life cycle inventories. *International Journal of Life Cycle Assessment*, **4**, 48–56.

59 Ekvall, T. and Andræ, A.S.G. (2006) Attributional and consequential environmental assessment of the shift to

lead-free solders. *International Journal of Life Cycle Assessment*, **11**, 344–353.

60 Langeveld, H., Sanders, J., and Meeusen, M. (2010) *The Biobased Economy: Biofuels, Materials and Chemicals in the Post-oil Era*, Earthscan, London.

61 European Commission (2012) Innovating for Sustainable Growth: A Bioeconomy for Europe, Brussels.

62 The White House (2012) National Bioeconomy Blueprint, Washington.

63 Bosch, R., van de Pol, M., and Philp, J. (2015) Policy: define biomass sustainability. *Nature*, **523**, 526–527.

64 Dale, B.E., Anderson, J.E., Brown, R.C., Csonka, S., Dale, V.H., Herwick, G., Jackson, R.D., Jordan, N., Kaffka, S., Kline, K.L. *et al.* (2014) Take a closer look: biofuels can support environmental, economic and social goals. *Environmental Science and Technology*, **48**, 7200–7203.

65 Kircher, M. (2012) The transition to a bio-economy: emerging from the oil age. *Biofuels, Bioproducts & Biorefining*, **6**, 369–375.

66 Pawelzik, P., Carus, M., Hotchkiss, J., Narayan, R., Selke, S., Wellisch, M., Weiss, M., Wicke, B., and Patel, M.K. (2013) Critical aspects on the life cycle assessment (LCA) of bio-based- materials – reviewing methodologies and deriving recommendations. *Resources, Conservation and Recycling*, **73**, 211–228.

67 Ciriminna, R., Pina, C.D., Rossi, M., and Pagliaro, M. (2014) Understanding the glycerol market. *European Journal of Lipid Science and Technology*, **116**, 1432–1439.

68 Ayoub, M. and Abdullah, A.Z. (2012) Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry. *Renewable and Sustainable Energy Reviews*, **16**, 2671–2686.

69 Morales, M., Dapsens, P.Y., Giovinazzo, I., Witte, J., Mondelli, C., Papadokonstantakis, S., Hungerbuhler, K., and Perez-Ramirez, J. (2015) Environmental and economic assessment of lactic acid production from glycerol using cascade bio- and chemocatalysis. *Energy and Environmental Science*, **8**, 558–567.

70 ecoinvent (2010) Life Cycle inventory database v2.2 (Dübendorf, CH: Swiss Centre for Life Cycle Inventories).

71 Cespi, D., Passarini, F., Mastragostino, G., Vassura, I., Larocca, S., Iaconi, A., Chieregato, A., Dubois, J.L., and Cavani, F. (2015a) Glycerol as feedstock in the synthesis of chemicals: a life cycle analysis for acrolein production. *Green Chemistry*, **17**, 343–355.

72 Cespi, D., Passarini, F., Vassura, I., and Cavani, F. (2015b) Butadiene from biomass, a life cycle perspective to address sustainability in the chemical industry. *Green Chemistry*, **18**, 1625–1638.

73 Chen, G.-Q. and Patel, M.K. (2012) Plastics derived from biological sources: present and future: a technical and environmental review. *Chemical Reviews*, **112**, 2082–2099.

74 Cherubini, F. and Jungmeier, G. (2009) LCA of a biorefinery concept producing bioethanol, bioenergy, and chemicals from switchgrass. *The International Journal of Life Cycle Assessment*, **15**, 53–66.

75 Moncada, J., Posada, J.A., and Ramírez, A. (2015) Early sustainability assessment for potential configurations of integrated biorefineries. Screening of bio-based derivatives from platform chemicals. *Biofuels, Bioproducts & Biorefining*, **9**, 722–748.

76 Nuss, P. and Gardner, K.H. (2013) Attributional life cycle assessment (ALCA) of polyitaconic acid production from northeast US softwood biomass. *The International Journal of Life Cycle Assessment*, **18**, 603–612.

77 Posada, J.A., Patel, A.D., Roes, A., Blok, K., Faaij, A.P.C., and Patel, M.K. (2013) Potential of bioethanol as a chemical building block for biorefineries: preliminary sustainability assessment of 12 bioethanol-based products. *Bioresource Technology*, **135**, 490–499.

78 Vink, E.T.H., Davies, S., and Kolstad, J. (2010) The eco-profile for current Ingeo® polylactide production. *Industrial Biotechnology*, **6**, 212–224.

79 Weiss, M., Patel, M., Heilmeier, H., and Bringezu, S. (2007) Applying distance-to-target weighing methodology to evaluate the environmental performance of bio-based energy, fuels, and materials. *Resources, Conservation and Recycling*, **50**, 260–281.

80 Kamm, B., Gruber, P.R., and Kamm, M. (2006) *Biorefineries: Industrial Processes and Products – Status Quo and Future Directions*, **1**, Wiley-VCH Verlag GmbH, Weinheim.

81 Kamm, B. and Kamm, M. (2004) Principles of biorefineries. *Applied Microbiology and Biotechnology*, **64**, 137–145.

82 Bringezu, S., Schütz, H., Pengue, W., O'Brien, M., Garcia, F., Sims, R., Howarth, R., Kauppi, L., Swilling, M., and Herrick, J. (2014) *Assessing Global Land Use: Balancing Consumption with Sustainable Supply*. In a report of the Working Group on Land and Soils of the International Resource Panel. UNEP International Resource Panel, Paris.

83 IEA (2015) IEA Bioenergy Task 42 Biorefinery. In International Energy Agency (IEA) Bioenergy.

84 Hayes, D.J. (2009) An examination of biorefining processes, catalysts and challenges. *Catalysis Today*, **145**, 138–151.

85 Nuss, P., Bringezu, S., and Gardner, K.H. (2012) Waste-to-materials: the longterm option, in *Waste to Energy: Opportunities and Challenges for Developing and Transition Economies* (ed. A. Karagiannidis), Springer, London, pp. 1–26.

86 Cherubini, F. (2010) The biorefinery concept: using biomass instead of oil for producing energy and chemicals. *Energy Conversion and Management*, **51**, 1412–1421.

87 Bringezu, S., Schütz, H., ÓBrien, M., Kauppi, L., Howarth, R.W., and McNeely, J. (2009b) *Towards Sustainable Production and Use of Resources: Assessing Biofuels*. In UNEP Resource Panel, UNEP, Paris, pp. 120.

88 Cordell, D., Drangert, J.-O., and White, S. (2009) The story of phosphorus: global food security and food for thought. *Global Environmental Change*, **19**, 292–305.

89 Souza, D.M., Teixeira, R.F.M., and Ostermann, O.P. (2015) Assessing biodiversity loss due to land use with life cycle assessment: are we there yet? *Global Change Biology*, **21**, 32–47.

90 Teixeira, R.F.M., Maia de Souza, D., Curran, M.P., Antón, A., Michelsen, O., and Milà i Canals, L. (2015) Towards consensus on land use impacts on biodiversity in LCA: UNEP/SETAC life cycle Initiative preliminary recommendations based on expert contributions. *Journal of Cleaner Production*, **112**, 4283–4287.

91 Graedel, T.E., Harper, E.M., Nassar, N.T., Nuss, P., and Reck, B.K. (2015) Criticality of metals and metalloids. *Proceedings of the National Academy of Sciences of the United States of America*, **112**, 4257–4262.

92 Searchinger, T., Heimlich, R., Houghton, R.A., Dong, F., Elobeid, A., Fabiosa, J., Tokgoz, S., Hayes, D., and Yu, T.-H. (2008) Use of U.S. croplands for biofuels increases greenhouse gases through emissions from land-use change. *Science*, **319**, 1238–1240.

93 Searchinger, T.D., Hamburg, S.P., Melillo, J., Chameides, W., Havlik, P., Kammen, D.M., Likens, G.E., Lubowski, R.N., Obersteiner, M., Oppenheimer, M. *et al.* (2009) Fixing a critical climate accounting error. *Science*, **326**, 527–528.

94 McKechnie, J., Colombo, S., Chen, J., Mabee, W., and MacLean, H.L. (2011) Forest bioenergy or forest carbon? Assessing trade-offs in greenhouse gas mitigation with wood-based fuels. *Environmental Science & Technology*, **45**, 789–795.

95 Walker, T. (2010) Massachusetts Biomass Sustainability and Carbon Policy Study. Report to the Commonwealth of Massachusetts Department of Energy Resources, in Natural Capital Initiative Report, Manomet Center for Conservation Science, Brunswick, Maine.
.

96 Levasseur, A., Brandão, M., Lesage, P., Margni, M., Pennington, D., Clift, R., and Samson, R. (2012) Valuing temporary carbon storage. *Nature Climate Change*, **2**, 6–8.

97 Johnson, E. (2009) Goodbye to carbon neutral: getting biomass footprints right. *Environmental Impact Assessment Review*, **29**, 165–168.

98 Amazega, J.M., von Maltiz, G., and Boyes, S. (2010) *Assessing the Sustainability of Bioenergy Projects in Developing Countries: A framework for Policy Evaluation*, Newcastle University, England.

99 Milà i Canals, L., Bauer, C., Depestele, J., Dubreuil, A., Freiermuth Knuchel, R., Gaillard, G., Michelsen, O., Müller-Wenk, R., and Rydgren, B. (2007) Key elements in a framework for land use impact assessment within LCA (11 pp) *The International Journal of Life Cycle Assessment*, **12**, 5–15.

100 Koellner, T., de Baan, L., Beck, T., Brandão, M., Civit, B., Margni, M., i Canals, L., Saad, R., de Souza, D., and Müller-Wenk, R. (2013) UNEP-SETAC guideline on global land use impact assessment on biodiversity and ecosystem services in LCA. *The International Journal of Life Cycle Assessment*, **18**, 1188–1202.

101 Brandão, M., Levasseur, A., Kirschbaum, M.U.F., Weidema, B.P., Cowie, A.L., Jørgensen, S.V., Hauschild, M.Z., Pennington, D.W., and Chomkhamsri, K. (2013) Key issues and options in accounting for carbon sequestration and temporary storage in life cycle assessment and carbon footprinting. *The International Journal of Life Cycle Assessment*, **18**, 230–240.

102 Christensen, T.H., Gentil, E., Boldrin, A., Larsen, A.W., Weidema, B.P., and Hauschild, M. (2009) C balance, carbon dioxide emissions and global warming potentials in LCA-modelling of waste management systems. *Waste Management & Research*, **27**, 707–715.

103 Cherubini, F., Bird, N.D., Cowie, A., Jungmeier, G., Schlamadinger, B., and Woess-Gallasch, S. (2009) Energy- and greenhouse gas-based LCA of biofuel and bioenergy systems: key issues, ranges and recommendations. *Resources, Conservation and Recycling*, **53**, 434–447.

104 Bringezu, S., Schütz, H., Arnold, K., Merten, F., Kabasci, S., Borelbach, P., Michels, C., Reinhardt, G.A., and Rettenmaier, N. (2009a) Global implications of biomass and biofuel use in Germany – recent trends and future scenarios for domestic and foreign agricultural land use and resulting GHG emissions. *Journal of Cleaner Production*, **17**, S57–S68.