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Developing a Framework for Achieving Global Carbon Dioxide Removal with Bio-based
Plastics

By

ELISABETH VAN ROIJEN
DISSERTATION

Submitted in partial satisfaction of the requirements for the degree of

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Abstract:

Limiting the rise of global mean temperatures and stabilizing Earth's climate will require achieving net-zero emissions of long-lived greenhouse gases (GHGs) [1]. However, ongoing (residual) emissions from difficult-to-decarbonize sources, such as those from chemical reactions for commonly used products, [2,3] will need to be balanced by removal of carbon dioxide (CO₂) or other GHGs from the atmosphere (hereinafter "CDR") [4]. Enabling CDR via materials is a logical first step given the already large and growing demand for materials, eliminating the need to develop new industries for CDR. One such hard-to-carbonize material is plastic, with 99% of plastic materials made from fossil fuels. Driven by growing single-use consumer applications, the rate at which plastics are produced and disposed of is outpacing most other human-made materials.

Producing plastic from bio-based feedstocks is a commonly discussed method to mitigate impacts of fossil-based plastic production and, more recently, act as a CDR mechanism. In this work, numerous pathways that could support bio-based plastics acting as a CDR strategy on a global scale by 2050 are presented. Due to their high technology-readiness and to promote a circular bioeconomy, this study focuses on the utilization of non-edible biomass resources as feedstocks for plastic production, rather than the formation of plastics from CO₂ capture and utilization. Pathways are presented which consider the level of bio-based plastic market replacement, the type of energy resources used for production, as well as the prevalence of different waste management practices to systematically assess what levers need to be pulled to enable CDR in plastics. Production pathways and associated life cycle inventories for bio-based plastics from 2nd and 3rd generation feedstocks resulting in CDR are derived.

To model end-of-life (EoL) impacts, a review is conducted to examine the biodegradation behavior and associated GHG emissions from bio-based plastics in different environments. Findings from this work suggest that various combinations of strategies could be employed to achieve CDR in plastics, with the greatest uptake from the scenarios considered leading to ~260 Mt of annual CDR by 2050. Considering resource availability and technological characteristics, a roadmap is generated to evaluate the feasibility of bio-based plastics acting as a CDR pathway.

Building from this foundation, this research expands beyond the carbon storage potential of plastics to examine the scale of CO₂ that might be stored annually in consumed construction materials and finds that fully replacing conventional building materials with CO₂-storing alternatives could sequester 19.3 Gt of CO₂ each year, which is roughly 50% of anthropogenic CO₂ emissions emitted in 2021. This work presents a framework to analyze full lifecycle emissions of materials and determine the carbon sequestration potential utilizing a time-dependent global warming calculation. This framework allows for consistent comparisons across materials and emissions mitigation strategies at varying lifecycle stages, and it can be adapted to calculate the CDR potential for other materials with different lifespans and applications. The flexibility of this method, and the ability to identify GHG emission hot-spot lifecycle stages, will be instrumental in identifying pathways to achieve CDR through materials production.

Chapter 1. Introduction

To ensure a livable future, global decarbonization needs to occur. This decarbonization requires eliminating greenhouse gas (GHG) emissions from various sectors including transportation, energy generation, and materials production. As populations rise and economies advance, these sectors are going to continue contributing to global GHG emissions and further narrow the existing carbon budget, or the total amount of anthropogenic CO₂ that can still be emitted while staying below 1.5°C warming from pre-industrial levels. The Intergovernmental Panel on Climate Change (IPCC) predicts that we are on track to exceed the 1.5°C warming target, and society would need to achieve a 100% reduction in annual GHG emissions by 2050 to stay below 1.5°C warming [1]. Although there are roadmaps and targets set in place for electrifying and decarbonizing transportation and energy grids, such as the International Energy Agency's roadmap to net-zero energy by 2050 [5], there are a number of other hard-to-decarbonize sectors. One such example is materials production. Materials like cement, steel, and plastic are hard to decarbonize because they have inherent process-based emissions, in addition to energy-derived emissions (**Figure 1**). For example: cement production involves the calcination of limestone, which is a high-temperature process that releases CO₂ emissions; steel production relies on fossil fuel inputs (coal or natural gas) for the reduction of iron ore, which releases CO₂ as a byproduct; and the production of plastics utilizes fossil-fuel feedstocks for polymerization, which can be both energy and CO₂-intensive. As a result, materials production resulted in 11 billion tons of carbon dioxide equivalent (CO₂e) emissions in 2015 [6]. At the same time, we know these materials are vital to society; cement and steel serve as the foundation of our built environment, while plastics are utilized in all aspects of society from transportation to food packaging. Therefore, there is a drastic need to alter the production methods of these materials to meet the

demands and living standards of future generations without contributing to irreversible climate change damages.

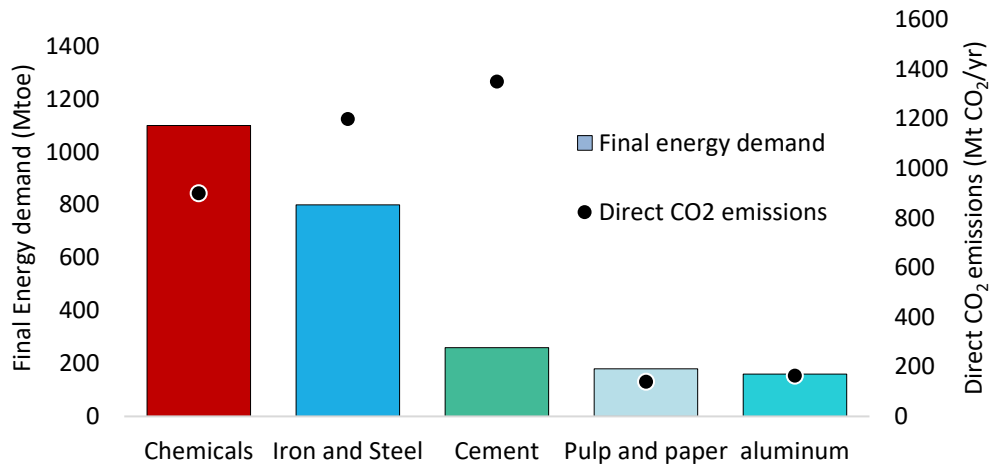


Figure 1 Final energy demand (in Mtoe) and direct CO₂ emissions (in Mt CO₂/year) for various materials. Source data obtained from [7].

Even if many sectors work to decarbonize and reach net-zero anthropogenic CO₂ emissions, global warming will have long-lasting impacts that can cause irreversible damage to ecosystems. Therefore, in addition to achieving net-zero emissions, due to the long lifetime of GHG emissions, CO₂ removal technologies must be implemented to mitigate the long-lasting impacts of climate change. In this work, the potential to utilize feedstocks in the materials industry as a method for carbon dioxide removal (CDR) is explored. A case study is performed on using bio-based feedstocks in the plastic sector. The plastic sector is of special interest given that the growth in plastic production has outpaced all other bulk materials [7] and is projected to triple by 2060 [8]. Further, the carbon footprint of the plastic sector is notable due to high energy-demands and a reliance on fossil fuel feedstocks, contributing to what is projected to be 15% of the carbon budget by 2050 [9]. Beyond production-related emissions, waste management of plastics continues to be a problem with 79% of all plastics ever made ending up in landfills or in the environment [10]. Due to this mismanagement of plastic waste, it is anticipated there will be

more plastics in our oceans than fish by the year 2050 [11]. Further, even if current policies to reduce plastic pollution are implemented, it is estimated that half of all plastic waste would still be landfilled in 2060 [8]. In addition to landfilling, the lack of access to proper waste management facilities in developing economies, effecting nearly 2 billion people globally, results in open burning of plastics which has significant CO₂ emissions, as well as toxic heavy metal emissions which can have negative impacts on human health [12]. This linear economy not only drives increased production of virgin fossil-based plastics, but it also results in the formation of microplastic pollution which can have negative impacts on human health and ecosystems [13].

Bio-based plastics, or plastics made from bio-based feedstocks, have the potential to reduce plastics production-side GHG emissions due to the photosynthetic uptake of CO₂ during biomass cultivation. Further, bio-based plastics that are biodegradable, and can therefore be broken down back into organic matter via aerobic or anaerobic biodegradation, have the ability to create a more circular economy for plastics and minimize pollution. In this study, the potential to utilize bio-based feedstocks, rather than fossil-fuels, as a source for plastic production is examined. Previous studies have highlighted the potential for plastics to act as a carbon sink via the utilization of 100% renewable energy, 100% recycling rates, and 100% bio-based plastics [9]. Similarly, various regional and international targets have been set to limit plastic pollution or increase the bio-based content of plastic materials. For example, the United States has set forth a goal to achieve 90% bio-based plastics by 2040 [14], and the United Nations has targets for achieving 50% recycling rate of plastics by 2030 [15]. However, given the massive scale of plastic production, and the multitude of issues surrounding plastic disposal and pollution, a

number of questions need to be addressed to determine the suitability of bio-based plastics as a replacement for fossil-based plastics: (1) What are the environmental impacts of bio-based plastic production? How do the GHG emissions of bio-based plastic production compare to fossil-based plastics? (2) Do sufficient bio-based resources exist to meet global plastic demand? If so, what feedstocks can be utilized that minimize competition with food? (3) What are the impacts of bio-based plastic disposal? What are the trade-offs between biodegradable and non-biodegradable bio-based plastics? What changes need to be made to the waste management system of plastics to achieve climate change mitigation goals? This work aims to address these questions and derive a framework for understanding the potential for CDR in materials. In addition, a roadmap for how to shift the plastic sector from acting as a significant carbon source to a carbon sink is demonstrated. A general overview of the framework utilized to achieve the above research questions is presented in **Figure 2**.

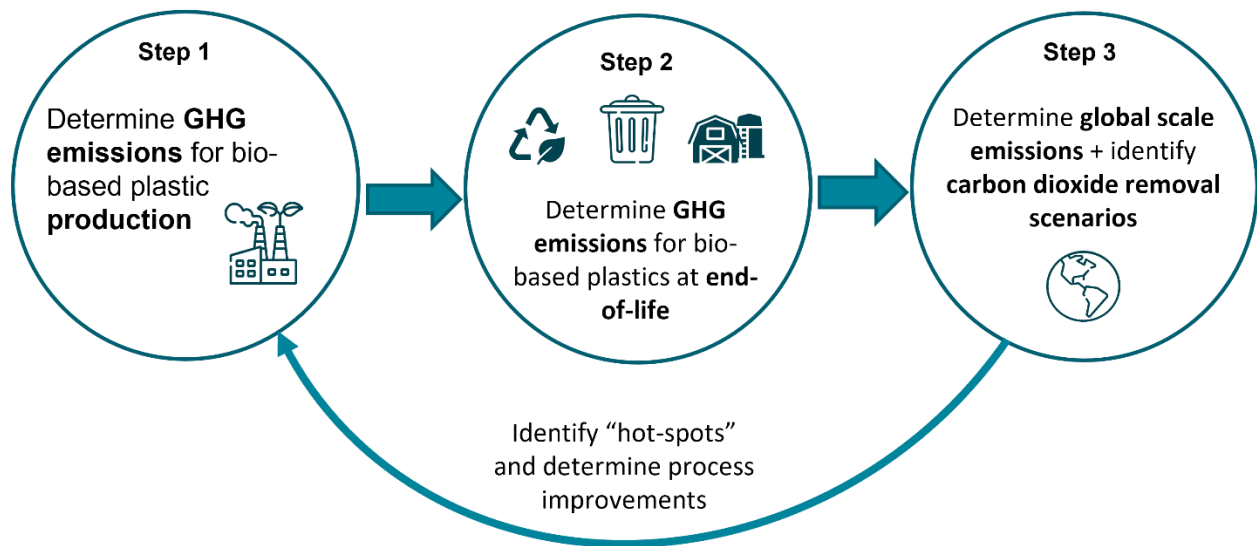


Figure 2 Flow diagram of framework

Life cycle assessments (LCAs) are a common methodology to determine the environmental impacts of a given product or process by accounting for the impacts associated with each life cycle stage, from raw material acquisition to disposal [16]. Previous LCA literature regarding the life cycle impacts of bio-based plastic production has resulted in mixed conclusions due to variations in methodological approaches, data sources, and assumptions [17]. Therefore, this work fills an important research gap by providing a consistent, bottom-up model for determining the GHG emissions of bio-based plastic production. Further, bio-based, biodegradable plastics offer the possibility to avoid some of the negative impacts of plastic pollution by enabling a circular pathway in which materials biodegrade (either aerobically or anaerobically) back into CO₂, H₂O, CH₄ and organic matter. However, the extent and rate that these materials biodegrade in our current waste management systems (e.g. landfills, compost, and anaerobic digestion systems), and the associated GHG emissions, varies greatly depending on various environmental conditions and bio-based plastic properties. Further, emissions associated with bio-based plastic biodegradation may reduce the CDR potential of these materials. Therefore, this work captures the uncertainty and variability associated with end-of-life impacts of bio-based, biodegradable plastics by harnessing data from experimental results and calculating associated impacts.

The ability to sequester carbon using bio-based resources is not limited to plastic materials. In fact, bio-based feedstocks can be substituted across various materials in our built environment including concrete, brick, and asphalt. Utilizing bio-based feedstocks in the built environment also provides an avenue for temporary carbon storage due to the long use-phase of these materials. Therefore, this study builds off the bio-based plastic case study to examine the theoretical carbon storage potential of all building materials (with some extension to published

carbon mineralization pathways). However, given that building materials have a long use-phase, meaning production and end-of-life emissions can occur decades apart, it is also important to consider the impact of emissions timing on cumulative radiative forcing. The lifecycle impacts of materials are typically determined using a traditional global warming potential (GWP) calculation, wherein emissions are summed together and assumed to occur within the same year. This work therefore fills an important research gap by developing a tool that can be used to determine the impact of dynamic emissions on the carbon storage potential of any material or process. This work serves as a foundation for future scientific developments around CDR potential in existing materials and novel technologies.

In Chapter 2, the methods and results of systematic cradle-to-gate life cycle assessments of bio-based plastics, capable of substituting 80% of current fossil-based plastics, are described. This is done by harmonizing life cycle inventory data from various literature sources and existing datasets, applying consistent methods, and utilizing similar data sources across all materials to minimize temporal and regional variation. As part of this assessment, the GHG emissions associated with bio-based plastic production from 1st generation, or food-crops, as well as 2nd and 3rd generation, or non-edible feedstocks are determined. The incorporation of renewable electricity and bioenergy for bio-based plastic production is examined to determine the potential for this class of materials to act as a carbon sink. Environmental hot-spots, outside of energy-related emissions, associated with bio-based plastic production are identified to highlight areas for future research that could help further increase the carbon sequestration potential of plastics. Finally, the impact of LCA methodologies, such as allocation methods, are investigated, to understand the sensitivity of results to user inputs/decisions.

In Chapter 3, the behavior of bio-based biodegradable plastics in different end-of-life environments and their associated GHG emissions is summarized. Data regarding the extent of biodegradation achieved, and the associated GHG emissions are collected and summarized. A meta-analysis of experimental biodegradation studies is conducted to inform modelling inputs and capture the variability and heterogeneity of biodegradation behavior. Comparisons are drawn between the results of experimental studies and the modelled end-of-life impacts in life cycle assessment studies, to highlight sources of discrepancy. This work fills a key research gap of understanding how a shift to bio-based plastics, with biodegradable materials making up roughly 20% of the future plastic market [18,19], might influence future end-of-life impacts of plastics and the overall CDR potential of the plastic market.

In Chapter 4, various pathways that lead to bio-based plastics acting as a global-scale CDR mechanism are presented. These scenarios highlight the potential flexibility in the energy grid, waste management system, and types of feedstocks that could be harnessed to achieve CDR on a global scale. Key thresholds are identified to determine the minimum amount of bio-based plastics, recycled plastics, and renewable energy that needs to be achieved to reach net-negative emissions. Identifications of these thresholds is extremely pertinent for policy makers and relevant stakeholders to understand necessary advancements. Further, an assessment of the availability of resources and the technological readiness of the proposed solutions is leveraged to generate a roadmap to achieve net-negative emissions (i.e., CDR) for the plastic sector by 2050.

In chapter 5, the theoretical potential for other materials in the built environment to act as a carbon sink is demonstrated. A resource availability assessment is conducted to determine

the feasibility of leveraging the built environment as a carbon sink. The quantity of CO₂ removal potential for these materials is compared to the necessary CDR targets specified in the IPCC report [1]. Further, a comprehensive assessment tool is presented, which accounts for the dynamic timing of emissions uptake and release throughout a material's lifecycle to determine the carbon storage potential of a material. The outputs of the tool provide a breakdown of lifecycle stage emissions which can help to identify GHG emissions hotspots and opportunities for greater CDR potential. Furthermore, given that the global assessment of CDR in plastics presented in this dissertation focuses solely on emissions occurring within one year, this tool can be integrated in future work to better understand the impacts of dynamic emissions within the plastic industry, particularly for plastics used in long-lifetime applications.

This work outlines a framework that can be utilized for the development of carbon sink materials. A case study is performed on the plastic sector to demonstrate the ability of bio-based feedstocks, along with appropriate waste management techniques and process improvements, to contribute to CDR globally. The results from this study highlight specific targets that need to be achieved for the plastic sector to become a CDR mechanism and summarizes sources of variability and areas for future research to better understand the global impact of this class of materials. Finally, the capability of such methods is demonstrated through the theoretical determination of the carbon storage capacity of all building materials. Together, this work serves as a foundation for policymakers, relevant stakeholders in industry, and researchers to realize the potential to shift the materials industry to a carbon sink and help achieve necessary climate change mitigation goals.

Chapter 2. Identifying cradle-to-gate impacts of bio-based plastics

Authors note: This chapter comes from the publication “Towards the production of net-negative greenhouse gas emission bio-based plastics from 2nd and 3rd generation feedstocks” published in the *Journal of Cleaner Production*, vol 445, p.141203, 2024, doi:10.1016/j.jclepro.2024.141203.

Abstract:

Here, we show production pathways for CDR plastics from 2nd and 3rd generation feedstocks. We focus on bio-based plastics that are technically capable of replacing 80% of the global plastic market. By presenting life cycle inventories and discussing GHG-emissions hotspots, this work will inform stakeholders along the plastic supply chain of the necessary steps to achieving net-zero emissions by 2050, and potentially, how to drive net-uptake. This work is of critical importance given the overwhelming mass of plastic produced annually and the resulting CO₂ emissions. To conduct this assessment, we derive life cycle inventories for nine different bio-based plastics and address the impact of methodological choices, such as allocation method, on the resulting 100a global warming potential (GWP). Our findings show that resources used and processing methods implemented have significant effects on the potential for us to derive carbon-negative plastics. Furthermore, we find that environmental impact quantification methods greatly influence the perceived GWP of such processes. For example, economic and mass allocation methods resulted in an apparent increase in GWP of up to 39% and 166%, respectively, compared to no allocation for bio-based plastics made from 2nd generation crops, whereas mass allocation resulted in the lowest GWP for bio-based plastics made from 1st generation crops. In considering environmental impact hotspots, our findings show that decarbonization of thermal energy and electricity, reduced use of ammonia-based fertilizer, renewable hydrogen production, use of bio-based alternatives for petrochemicals and

plasticizers, enzyme production pathways from 2nd generation crops, and more efficient biomass conversion processes to reduce feedstock inputs may be critical steps in creating CDR bio-based plastics in the future.

1. Introduction

The mass of plastics in use today amounts to twice the mass of all animals on earth - 99% of which is made from fossil-based feedstocks [20,21]. The petrochemical industry as a whole is responsible for 18% of global industrial greenhouse gas (GHG) emissions, making it the third largest CO₂-emitting industry [7]. While many efforts have been taken to decarbonize common materials such as concrete [22–25] and steel [4,26–28], the methods for plastic production and disposal have remained largely the same. Minimizing the demand for plastics would help alleviate some of these issues, but consumption trends indicate plastics will continue to play a vital role in our economy in the coming years. In fact, plastics may contribute a significant role in the global transition to net-zero emissions by 2050 through their use in renewable energy, electric vehicles, medical devices, food packaging, and many other applications. Therefore, there is a need to identify strategies that allows for the continued growth of plastics while simultaneously mitigating GHG emissions from their production, and ideally converting this growing class of materials to becoming a pathway to carbon dioxide removal (herein referred to as “CDR plastics”).

Various studies have examined the potential for plastics to act as a carbon sink and although the methodologies and scopes differ, the same general conclusion is reached: there is no single solution to achieve CDR plastics. Initial exploration of decarbonization of fossil-based plastics

have indicated that achieving net-zero emissions, let alone net-negative, will be a challenge. Even with the use of renewable energy and recycling, there are several “carbon lock-ins” associated with fossil-based plastic production, such as emissions from steam cracking, that require carbon capture technology to achieve net zero emissions [29]. Frequently, bio-based plastics, which use biomass as the carbon feedstock instead of petroleum resources, have been examined as a way to reduce GHG emissions [17,30,31]. Authors who have explored these pathways still note potentially high emissions from energy-intensive production processes [32] and land-use change [33,34], changes in material performance that can alter use-phase impacts [35,36], and end-of-life pathways that could lead to GHG emissions, such as incineration or biodegradation [37]. As such, findings indicate that the transition to CDR plastics will require a combination of process electrification, improved waste management, as well as the use of non-edible biomass feedstocks [38].

Recent studies have indicated pathways worthy of deeper exploration when deriving CDR plastics. Sun *et al.* [39] examined pathways to reach carbon-neutral plastics and found that the use of biomass contributed the most to GHG reductions, with remaining strategies such as recycling only contributing 5-7%. Zibunas *et al.* [40] found that combining renewable energy with increased recycling rates of plastics could drive down emissions, but it would result in the highest cost compared to strategies that utilize biomass. Stegmann *et al.* [41], incorporated socio-economic factors to determine future CO₂ emissions from plastics and found that a combination of increased CO₂ prices, plastic recycling, and biomass use, could lead to carbon-negative approaches for plastic manufacturing. Similarly, Meys *et al.* [42] found that combining recycling, biomass utilization, and carbon capture and utilization (CCU) could lead to net-carbon-negative plastics that have lower cost and energy demands than fossil-based plastics with

CCU. While findings have been promising, many of these studies have only considered CO₂ emissions. However, to reach the Intergovernmental Panel on Climate Change (IPCC) targets of 1.5°C by 2050, a 50% and 22% reduction in CH₄ and N₂O must simultaneously be achieved alongside decarbonization strategies [43]. Considering the role of chemicals in biomass cultivation and plastic production, it is critical to understand the impact of other GHGs (e.g., N₂O from fertilizers [44]) on creating net-negative emissions pathways. In addition, most existing studies utilize models that rely on large data sets with life cycle assessment (LCA) data coming from various sources, thereby limiting the ability to (1) utilize a consistent approach among all materials, (2) determine what is contributing most to the environmental impacts of each material, and (3) determine how biomass feedstock type or LCA methodology can impact the results.

Carbon feedstock sources and modeling assumptions have been proven to play a large role in uptake potential for bio-based plastics in the literature [45]. Oliveiera *et al.* [46] performed bottom-up LCAs of bio-based plastics and found that carbon-negative bio-based plastics could be achieved when considering long-term applications (e.g., the use Bio-HDPE or Bio-PVC in construction). However, this study only examined 1st generation feedstocks which compete with food production. Deriving all plastics from such a resource would require roughly 5% of global arable land [47]. Alternatively, 2nd generation feedstocks, or inedible plant-based materials, and 3rd generation feedstocks, or feedstocks that have negligible land footprints (i.e. food waste, algae, or biogas), are being investigated in the literature as potential resources for bio-based plastic production. Given the extra processing steps required for utilizing these materials (e.g., pretreatment and enzymatic hydrolysis), it remains unclear if they could offer substantial GHG

emission reductions compared to 1st generation bio-based plastics or fossil-based plastics made from renewable energy. Studies have investigated the environmental impacts of bio-based plastics from 2nd and 3rd generation biomass such as corn stover [48–50], wheat straw [51], sugarcane bagasse [52], switchgrass [53], vetiver leaves [54], cheese whey [55,56], wastewater [57,58], landfill gas [59], and used cooking oil [60]. However, given the variability in methodologies, literature reviews of LCAs of bio-based plastics from 2nd and 3rd generation feedstocks report inconclusive results, with analyses considering the same 2nd generation feedstock leading to both higher and lower GHG emissions than their 1st generation counterpart [61]. Furthermore, transparent life cycle inventory (LCI) data are not consistently provided, limiting the ability to reproduce results [62]. To determine the large-scale impacts of a bio-based plastic economy, harmonization of data is necessary to support reproducible LCAs and to inform quantitative, systematic assessment of mechanisms to drive carbon-uptake.

In this work, we derive LCIs for nine major bio-based plastics: (1) polylactic acid (PLA); (2) polyhydroxyalkanoate (PHA); (3) thermoplastic starch (TPS); (4) high-density polyethylene (Bio-HDPE); (5) polyethylene terephthalate (Bio-PET); (6) polyvinylchloride (Bio-PVC); (7) polypropylene (Bio-PP); (8) polyurethane (Bio-PUR); (9) polytrimethyl terephthalate (Bio-PTT). All of these plastics at least partially utilize 2nd and 3rd generation feedstocks. We use these inventories to perform cradle-to-gate environmental impact assessments for each material. The influence of methodological decisions, namely the allocation method and hotspots in production that could be targeted to create carbon-negative plastics are analyzed. The term, “CDR plastics” refers to plastics with a below-zero value for the combined emissions of CO₂, CH₄ and N₂O with 100a global warming potentials (GWP) (other GHGs, such as water vapor and

hydrofluorocarbons, are outside the scope of this analysis due to their minimal impact on resulting GWP for the production processes examined herein [63,64]). Pathways to achieve CDR bio-based plastics and the remaining sources of GHG emissions are discussed to identify areas for further improvement.

2. Methods

2.1. Scope and goals

The goal of this work is to derive LCIs of plastics that can lead to CDR pathways during their production, assess methodological assumptions that could alter outcomes, and identify processes that should be targeted to drive emissions reductions. The functional unit for all inventories formulated in this work is 1 kg of bio-based plastic. The system boundary includes biomass cultivation, refinement, conversion, processing, and bio-based plastic production. The manufacturing of specific products (bottles, containers, etc.), the use phase, and end-of-life stage of bio-based plastics is not considered in this study. However, we note that the literature indicates these stages, specifically end-of-life, can contribute greatly to overall life cycle GHG emissions [37] and should be addressed in future work.

To create a systematic basis for inventory development, additional assumptions are made. Where possible, consistent LCI data sources are used for similar production processes, and when multiple LCI data sources exist, average values of the literature are used. We harmonize LCI flows and modeling assumptions to create a unified method for assessment and comparison of environmental impacts from bio-based plastics. Direct land use change associated with feedstock cultivation is included in these inventories. However, the inventories are based on an

attributional approach, and therefore do not include indirect impacts from land-use change. In the derivation of inventories, for non-biodegradable bio-based plastics, some downstream processes are identical to fossil-based plastics, and therefore are assumed to have the same process-based emissions, such as particulate matter emissions. To determine the feasibility of CDR bio-based plastics, all electricity and energy demands of the main processes are assumed to be satisfied by wind electricity and biogas. In addition, a biogenic carbon credit is applied based on the carbon content of the plastic. For example, if a plastic has a carbon content of 0.6 kg C/kg plastic, then a CO₂ credit of -2.2 kg CO₂ is applied (determined by multiplying the carbon content by the molar mass ratio of CO₂ to carbon, or 3.67 kg CO₂/kg C).

Three allocation methods were considered to determine the cradle-to-gate GHG emissions for each material: (1) mass, (2) economic, and (3) no allocation. With no allocation, main crops (such as corn) are assigned 100% of the impact, while any by-products (such as corn stover) are attributed 0%. While the International Organization for Standardization (ISO) recommends system expansion whenever possible [65], this method is outside the scope of this work. The life cycle CO₂-equivalents (CO₂e) for each material is determined based on CO₂, CH₄ and N₂O emissions. Global warming potentials of 28 and 273 are used for CH₄ and N₂O, respectively, based on the IPCC sixth assessment report [66].

2.2. Life cycle inventories of feedstocks

The following feedstocks are considered for bio-based plastic production: corn, corn stover, wheat straw, sugarcane sugar, sugarcane molasses, sugarcane bagasse, rapeseed oil, used cooking oil, reclaimed potato starch, and biogas. Sugarcane, corn, and wheat were considered in

this analysis given their abundant production volumes. Together, along with rice, these crops accounted for half of all primary crops produced globally in 2020 [67], with sugarcane and corn being the two most produced crops globally [67]. While palm oil and soybean oil are the largest produced vegetable oils [67], here we model rapeseed oil, making up 12% of global vegetable oil production in 2019. The selection of rapeseed oil for our inventories was due to the availability of detailed LCI data [68,69]. Data availability for soy [70] and palm-based polyol [71] LCAs have not been as robustly reported in the literature. We also consider 3rd generation feedstocks, such as landfill biogas, reclaimed potato starch, and used cooking oil. While many 3rd generation feedstocks have potential applications in bio-based plastics production, we again made the selection of these resources based on data availability.

We model biomass inventories based on large global producers of these crops. Land use requirements for every crop are determined by calculating the global weighted average crop yield from 2017 to 2020 using data from the Food and Agricultural Organization of the United Nations (FAO) [72]. The mass and economic allocation factors for each feedstock are determined from the literature (**Table 1**).

Table 1 Mass and economic allocation factors for the feedstocks considered in this study.

Feedstock type	Feedstock	Mass allocation factor	Economic allocation factor	Reference
1 st generation	Corn	0.50	0.86	Mass:[73] Economic: [74]
	Corn starch (from corn wet milling)	0.67	0.79	Mass:[75] Economic:[75,76]
	Rapeseed	0.23	0.5	Mass: [77] Economic: [78]
	Rapeseed oil	0.40	0.62	Mass:[77] Economic:[68,79]
	Sugar, from sugarcane	0.10	0.88	Mass:[80] Economic:[81–83]
2 nd generation	Molasses, from sugarcane	0.05	0.09	Mass:[80] Economic:[81–83]
	Bagasse, from sugarcane	0.31	0.03	Mass:[80] Economic:[81–83]
	Wheat straw	0.57	0.13	Mass:[73] Economic:[74,84]
	Corn stover	0.55	0.14	Mass:[85] Economic: [74]
3 rd generation	Used cooking oil	0	0	n/a
	Landfill biogas	0	0	n/a
	Reclaimed potato starch	0	0	n/a

For corn and corn stover production, we base our feedstock models on corn cultivation in the United States (US), the largest global producer of corn [72], with inventory values based on data from the ecoinvent 2.2 database [73]. To quantify production of stover, we assume 1 kg of corn stover is produced per kg of corn, as presented in the ecoinvent database. Although this value is representative of the US, it is close to the global average harvest index for corn, 0.45 kg corn/total biomass [85]. Some studies have found that 30-70% of the corn stover can be left on the field as a soil amendment to prevent erosion and maintain appropriate soil organic carbon levels [86–88]; therefore, we assume only 70% of corn stover is available for bio-based plastic production.

For sugarcane sugar, bagasse, and molasses, we base our feedstock models on Brazil, the world's largest producer of sugarcane [89]. This ecoinvent inventory is supplemented with agricultural

inputs such as fertilizer and pesticide use extracted from Seabra *et al.* (representative of the 2008/2009 growing season in Brazil) [90]. Data for sugarcane processing are from literature, using average values reported for Brazil [90,91], India [91], and Thailand [80], which are the three largest sugarcane-producing countries [89]. The yield of sugar from sugarcane is determined by taking the average values from studies by Groot and Boren (Thailand) [80] and Tsiropoulos *et al.* (India) [91]. We note that sugarcane mills commonly utilize the lignocellulosic by-product, bagasse, as an internal energy source. However, bagasse can be extracted for use in other applications (such as bioethanol or polylactic acid production), and here we aim to address potential benefits of use in bio-based plastics where the carbon can be stored for a longer period of time.

For wheat straw, LCI data for wheat cultivation, including yield ratios for wheat straw relative to grain, are taken from ecoinvent 2.2 [73]. This inventory is based on average values for wheat production in the US, the largest producer out of the countries available in the ecoinvent database for wheat production, and the fourth largest wheat producer globally [67]. The harvest index reported in this inventory, 0.45 kg wheat/total biomass, agrees with recent reported average values for wheat across the US [92]. Similar to corn stover, studies have shown that roughly 2/3 of wheat straw can remain on the field as a soil amendment [93]. Therefore, we assume only 1/3 of wheat straw is available for bio-based plastic production.

LCI data for rapeseed production is taken from Gupta *et al.* [77], which is representative of rapeseed production in Europe, the world's largest rapeseed oil producer [89]. The LCI data for agricultural processes, such as fertilizer and pesticide application rates, are based on rapeseed

production guidelines provided by New Holland Agriculture [94]. Large-scale rapeseed oil production data, reported in Gupta *et al.* [77], is based on industry data.

Potato starch can be retrieved as a residue from manufacturing sliced potato products, where starchy wastewater is generated, and starch can be extracted via centrifugation. For this carbon feedstock, we use LCI data for reclaimed potato starch from Broeren *et al.* [95]. Due to limited availability of data, the centrifugation process used to isolate the starch components is left out of the analysis. Broeren *et al.* found that this is a fair omission given that the energy requirements for this step are much lower than the subsequent evaporation steps that are captured in the inventory, and that it is part of the wastewater treatment process and, therefore, should be at least partly allocated to the primary product.

For landfill biogas as a feedstock for bio-based plastic production, we model the composition of landfill biogas based on a study by Rasi *et al.* [96]. It is assumed that if the biogas were not used as a feedstock for bio-based plastic production, then it would otherwise be burned. Therefore, the avoided CO₂ emissions from burning methane are applied as a credit (or negative emissions) to the system.

2.3. Life cycle inventories of bio-based plastic production processes

The various bio-based-plastic production pathways analyzed herein are outlined in **Figure 3**. Together, these bio-based plastics can substitute roughly 80% of today's fossil-based plastic market. To determine the substitution potential of each bio-based plastic within the current plastic market, we use the technical replacement potential of bio-based plastics reported by Shen

et al.[18], which is based on mechanical performance characteristics, coupled with the current global market of fossil-based plastics [19]. Sugarcane molasses is investigated as a feedstock for bioethanol production given that roughly 95% of molasses is currently used for ethanol production [91]. Both corn stover and wheat straw are modeled as feedstocks for bio-based ethanol, a key intermediate for Bio-HDPE, Bio-PET, and Bio-PVC production. Using a mass-based allocation approach with the life cycle inventories outlined herein, corn stover-based ethanol was found to have lower GHG emissions (3.7 kg CO_{2e}/kg ethanol, not including biogenic carbon) than wheat straw-based ethanol (5.97 kg CO_{2e}/kg not including biogenic carbon). Therefore, only corn stover-based ethanol is used for Bio-PET and Bio-PVC production. Corn is modeled as a feedstock for ethanol and lactic acid to allow for comparisons of environmental impacts between 1st, 2nd, and 3rd generation feedstocks. All electricity and heat requirements were assumed to be satisfied by wind and biogas (modeled using ecoinvent datasets outlined in Appendix A, supplemental data 0).

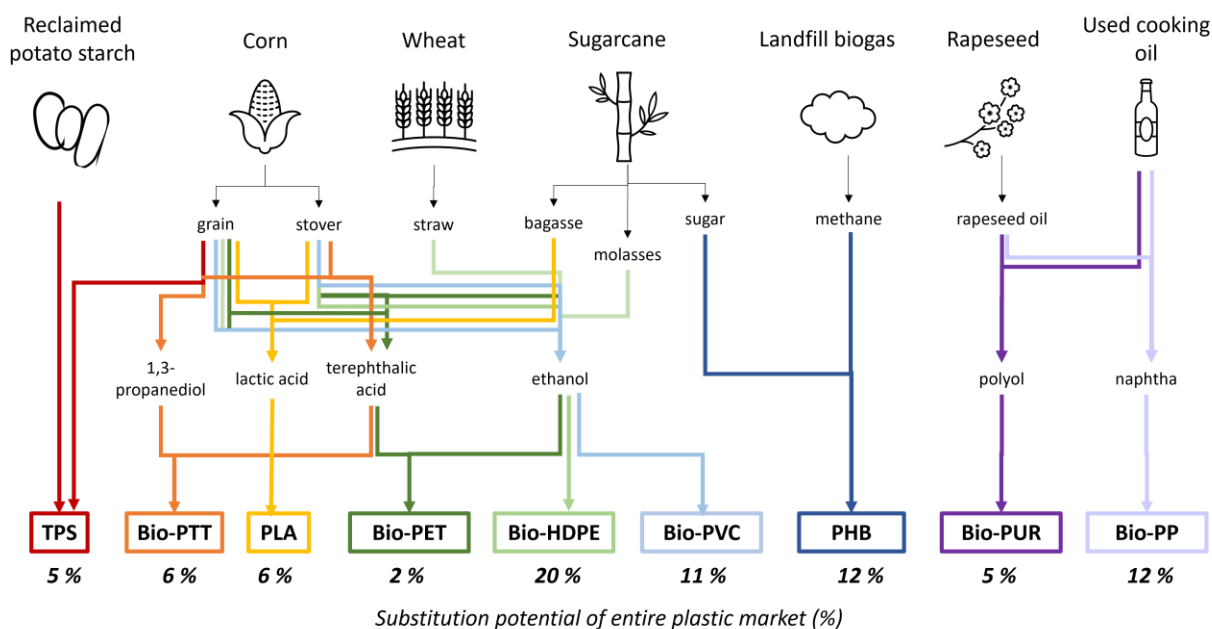


Figure 3. Overview of bio-based plastic production pathways examined in this study. This figure does not include all the process steps required for the conversion of feedstock to bio-based plastic, but rather highlights the general production routes with key

intermediates. The theoretical substitution potential of each bio-based plastic within the current fossil-based plastic market is presented underneath in italics. These values were obtained by combining the technical substitution potential of each bioplastic (based on material performance), with the current plastic market. Note that these substitution potentials are not reflective of the resource availability of the feedstocks used. Note the following acronyms: thermoplastic starch (TPS), polytrimethyl terephthalate (Bio-PTT), polylactic acid (PLA), polyethylene terephthalate (Bio-PET), high-density polyethylene (Bio-HDPE), polyvinylchloride (Bio-PVC), poly(3-hydroxybuturate) (PHB), polypropylene (Bio-PP), polyurethane (Bio-PUR).

2.3.1 LCIs for biodegradable bio-based plastics

PLA is a biodegradable, thermoplastic polyester that has been proposed as a substitute for traditional plastics such as polypropylene (PP), acrylonitrile butadiene styrene (ABS), polystyrene (PS), polyethylene (PE) and polyethylene terephthalate (PET), in food packaging and biomedical applications [97,98]. The LCI for PLA from corn is derived from NatureWorks, the largest global producer of PLA [99]. However, their published LCI data is highly aggregated and therefore difficult to modify. Therefore, we model the LCI for PLA from corn stover and sugarcane bagasse based on work by Ioannidou *et al.* [100] and Daful *et al.* [52], respectively. Producing lactic acid from lignocellulosic feedstocks involves four main steps. First, the feedstocks must be pre-treated, breaking down the biomass prior to enzymatic hydrolysis. LCI data for the pretreatment process of corn stover is based on a report from the National Renewable Energy Laboratory (NREL) on bioethanol production which includes two steps: (1) deacetylation and (2) dilute acid pretreatment. In this study, the LCI for this pretreatment process is slightly modified based on improvements to the design reported in a more recent report from NREL [101] (namely, reducing the loading of sulfuric acid from 22 mg/g dry solid to 9 mg/g dry solid). LCI data for the pretreatment of sugarcane bagasse is based on a steam explosion process. After pretreatment, the slurry is sent to a reactor for enzymatic hydrolysis using cellulase to convert cellulose into glucose. Glucose is then fermented to produce lactate. Traditionally, calcium carbonate is used as a neutralizing agent to reduce the negative effects of low pH on metabolic activities. However, in the LCI of bagasse-PLA, magnesium-hydroxide and triethylamine are

used for the neutralization process to reduce the generation of gypsum waste products [52]. To recover pure L-lactic acid, bacterial biomass is first separated from the fermentation broth via centrifugation, then the lactate is treated with 50% sulfuric acid to produce dilute lactic acid. Lactic acid is concentrated via evaporation and then reacted with methanol to produce methyl lactate. Finally, a distillation column is used for the hydrolysis of methyl lactate to produce polymer grade L-lactic acid. The LCI data for PLA production from lactic-acid via ring-opening polymerization reported in Ioannidou *et al.* [100] is based on a study by Gruber *et al.* [102]. Due to the lack of necessary data around reaction rates and the thermodynamics of intermediate products, the authors conducted a simulation of the components to calculate mass and energy balances of the process.

PHAs are microbially produced, readily biodegradable polyesters. They are suitable to replace traditional plastics in medical and food packaging applications, but scaling has been limited to date due to high costs of production [103]. One of the most common types of PHA, poly(3-hydroxybutyrate) (PHB), can be produced from either 1st or 3rd generation feedstocks using a similar process involving: (1) the accumulation of microbes in a reactor, (2) nutrient limitation (such as nitrogen or phosphorous) to form intracellular PHB, and (3) extraction of PHB from cells and purification. The LCI data for PHB production from sugar is based on Harding *et al.* [104], and the LCI data for PHB production from biogas is based on Rostkowski *et al.* [59]. We note that Rostkowski *et al.* [59] examined various extraction methods including solvent extraction, selective dissolution, and surfactant digestion. Solvent extraction was found to be the least favorable method in terms of GHG emissions, but is used in the LCI for this study to

remain consistent with the LCI for biogas-PHB and because it is the most commonly used PHB extraction method [105].

Starch is a widely abundant and cheap bio-based plastic, making up roughly 20% of global bioplastic production capacity [21], but to achieve desired properties it is typically blended at high temperatures with plasticizers to form TPS, making it only partially bio-based [106]. The LCI for TPS is based on the ecoinvent inventory for modified starch [73], which uses aggregated data from Novamont, the producer of a common TPS bioplastic called Mater-Bi [107]. This inventory is representative of TPS made from only 34% bio-based content. Here, starch is derived from corn wherein a milling process breaks down the corn into its components (corn starch, meal, germ, and feed). Mass allocation values reported in Ramirez *et al.* [75], are utilized in combination with market values reported by the United States Department of Agriculture [76] to determine economic allocation factors for this multi-output process. To model TPS production from reclaimed potato starch, the same inventory is used with reclaimed potato starch replacing corn starch.

2.3.2 LCIs of non-biodegradable bio-based plastics

Bioethanol is a common precursor in the production of bio-based, non-biodegradable plastics. We consider bioethanol production from two 2nd generation crops, corn stover and wheat straw, based on LCI data from Byun and Han [108] and Borrion *et al.* [93] respectively. The production of ethanol from lignocellulosic crops involves the following steps: (1) the hemicellulose fraction of the biomass is converted to xylose using sulfuric acid catalyst pretreatment; (2) the remaining fraction (cellulose) is converted into glucose using the cellulase enzyme; and then (3) the

biomass derived glucose is fermented with a yeast catalyst, corn steep liquor, and diammonium phosphate to produce an ethanol-rich stream. We also consider bioethanol production from corn and sugarcane molasses. The corn to ethanol conversion process is taken from Akanuma *et al.* [109]. The LCI data for molasses to ethanol conversion is adapted from Tsirpolous *et al.* [91] and is a simple process, which only requires fermentation and distillation steps to produce ethanol.

Here we model a fully bio-based PET LCI using data for the production of bio-based ethylene glycol and bio-based terephthalic acid (TPA) from corn stover using models from Chen *et al.* [53] and Benavides *et al.* [110]. We model TPA production from isobutanol intermediate - an established, high-volume commercial process. This process includes: (1) pre-treatment of corn stover to destruct lignocellulose into cellulose/hemicellulose; (2) enzymatic hydrolysis to convert polysaccharides into monosaccharides, which can be fermented into isobutanol; (3) conversion of isobutanol to paraxylene through dehydration, oligomerization, and dehydro-cyclination; and (4) oxidation of paraxylene into TPA. This final step results in the production of electricity and diesel blendstock, but these byproducts are considered outside of the scope of this work and all environmental impacts of these processing stages are attributed to the main product, TPA. The production of TPA from corn (based on Akanuma *et al.* [109]) is similar to corn stover derived TPA but without the pretreatment step. The LCI for bio-based ethanol from corn stover and corn are the same as discussed above, and the conversion process of ethanol to ethylene is based on Chen *et al.* [53]. The remaining processing steps (conversion to ethylene oxide, ethylene glycol and polymerization to PET) are identical to fossil-based plastic production processes, which we base onecoinvent 2.2 [73].

Bio-PVC is produced from the reaction between bio-based ethylene and chlorine. LCI data for PVC production is therefore the same as fossil-based PVC production, reported inecoinvent, with the exception that ethanol is derived from biomass using the methods described above, and again, the conversion process of ethanol to ethylene is based on Chen *et al.* [53].

We model Bio-PP production from a 3rd generation feedstock, used cooking oil, and 1st generation feedstock, rapeseed oil. The only difference between the two production routes is the upstream production of both used cooking oil and rapeseed oil. From there, the process starts with the pretreatment and de-oxygenation of oil, producing bio-based naphtha, a by-product of hydrotreated vegetable oil (HVO). The LCI data for this multi-output process is from Neste, a biorefinery located in the Netherlands [111]. Mass allocation is applied where HVO is the main product (91 wt%), followed by bio-propane (6 wt%), bio-naphtha (2 wt%), and water (1 wt%). Bio-based naphtha is then converted to smaller hydrocarbons (including propylene) via steam cracking. Given that steam cracking produces multiple products, mass allocation is applied. Ethylene is the major product when naphtha feedstock is used (35 wt%), followed by pyrolysis gas (20 wt%), methane (16 wt%), bio-propylene (14%), C4 (8%), pyrolysis fuel oil (5%) and hydrogen (2%). This process is assumed to be the same for both rapeseed oil and used cooking oil, given that both feedstocks result in HVOs with similar properties and yield similar products upon steam cracking [112]. Mass allocation factors for this steam cracking process are based on current US average industry data [113]. The final step of polymerization is identical to the fossil-based polymerization process, and we model this process basedecoinvent data [73].

Bio-PUR is modeled based on the conversion of rapeseed oil or used cooking oil to bio-based polyol via amidization with diethanolamine (DEA). The LCI data for the conversion process comes from a cradle-to-gate LCA study on rapeseed oil-based polyol production [69], and is assumed to be the same for used cooking oil. While it is possible to have transesterification of rapeseed oil/used cooking oil with triethanolamine, we model the DEA route due to its known lower GHG emissions. The LCI for the final step (the generation of polyurethane foam) is obtained fromecoinvent as it is assumed to be identical to fossil-based PUR foam production [73]. Given that the bio-based polyol content varies depending on the type of foam, both rigid and flexible PUR foam are modeled herein.

We model Bio-PTT production based on the two main ingredients, 1-3, propenadiol (PDO) and TPA. The LCI for PDO production from corn glucose was obtained from Urban and Bakshi [114], which involves a commercialized fermentation process using genetically engineered *E. coli*. The impacts from inoculum production are assumed to be negligible because once they are produced, they are self-sufficient, and the CO₂ emissions from glucose fermentation are determined stoichiometrically. The LCI for TPA production from corn stover is the same one that is used for Bio-PET. Given the similarities in chemical structure between PET and PTT, the electricity and heat requirements for the polymerization of PTT from PDO and TPA are assumed to be the same as PET.

3. Results

3.1 Greenhouse gas emissions and identifying environmental impact hotspots

Our findings show that it is possible to synthesize cradle-to-gate CDR bio-based plastics with appropriate selection of feedstock (**Figure 4**). Even though some of the bio-based plastics are partially fossil-based such as PUR and TPS, they are still able to reach GHG-negative emissions when renewable energy is used. Therefore, future increases in biomass content in bio-based plastics could offer the ability to uptake even more CO₂ during production and potentially drive greater GHG-negative fluxes. These negative fluxes are achieved primarily by satisfying all energy demands with renewable electricity and heat, coupled with the biogenic carbon storage in bio-based plastic. These pathways were selected as the means to reduce GHG emissions due to known energy contributions to plastics production [115] and the role of renewable carbon feedstocks on net-GHG emissions [116]. When utilizing the 2018 global average electricity mix (see Appendix A, supplemental data 1), along with traditional fossil-fuel heat sources such as coal and natural gas, energy-derived emissions are responsible for up to 96% of production emissions for these bio-based plastics (see Appendix A, supplemental data 19 for a detailed breakdown of process contributions without renewable energy). By nearly eliminating energy-related emissions through the use of renewables, life cycle GHG emissions can be up to 30 times lower for some bio-based plastics (as is the case for PLA from sugarcane bagasse). Similarly, the cradle-to-gate impacts for PHB from landfill biogas amounted to -0.53 and 11 kg CO_{2e}/kg with and without the use of renewable energy, respectively, when applying carbon credits in the form of avoided CO₂ (rather than avoided CH₄). Despite the potential for GHG-negative bio-based plastics, agricultural and chemical processes for bio-based plastics are still emissions intensive. Therefore, the following section provides a breakdown of the environmental impact hotspots that

exist when energy-related impacts are nearly eliminated. Noting that process modifications can help reduce these emissions [117], here we utilize a mass-based allocation approach to examine sources of these emissions, broadly categorized as: (1) “Agricultural emissions” for emissions related to the cultivation of agricultural feedstocks (agricultural machinery, direct land-use change, fertilizer inputs, irrigation, etc.); (2) “Energy emissions” for emissions associated with renewable energy use; (3) “Processing/conversion emissions” for emissions related to conversion of feedstocks to bio-based plastics (such as industrial chemical production); or (4) “Other emissions” for sources of emissions that contribute to less than 5% of the overall GHG emissions and therefore are not examined on an individual basis.

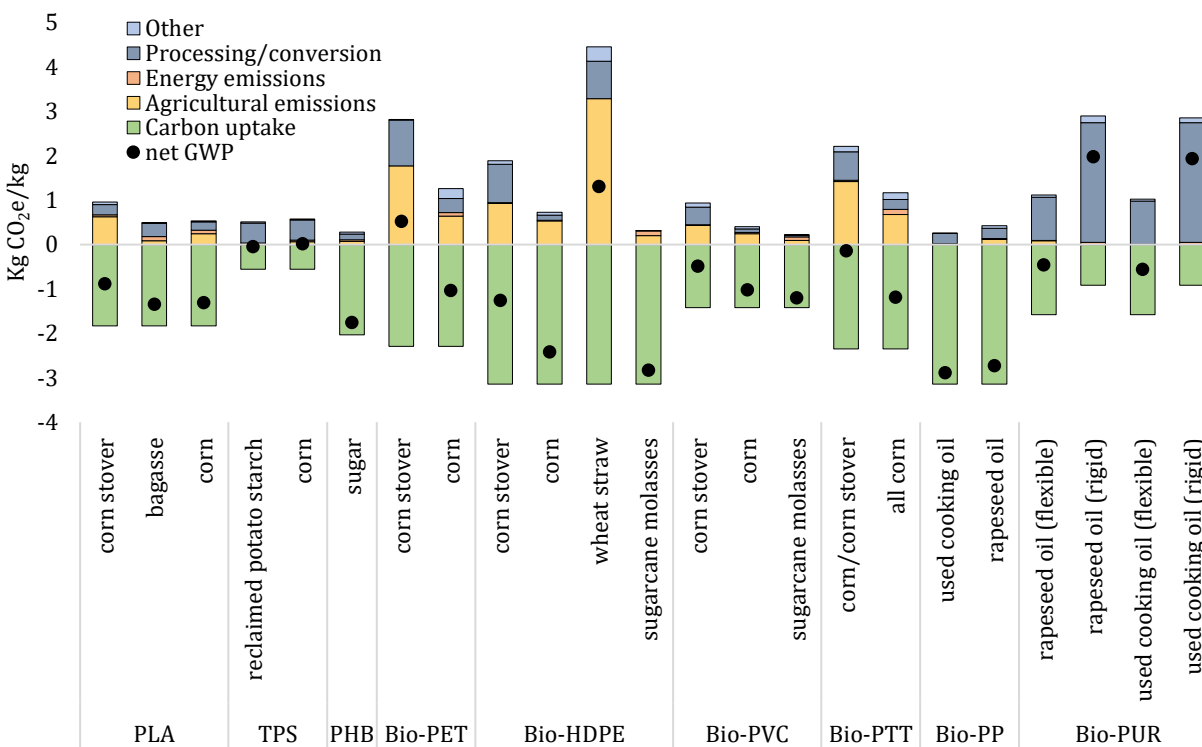


Figure 4 Process contributions for cradle-to-gate GHG emissions of bio-based plastics using a mass-allocation approach. Process contributions are broken down by carbon uptake (green), agricultural processes (yellow), energy emissions (orange) from renewable energy, processing and conversion (blue/gray), and “other” processes contributing to less than 5% of overall emissions (light blue). Net GWP is shown by the black dots. GWP (or CO₂e) is calculated using GWP factors for CO₂, CH₄ (28) and N₂O (273) emissions. Note the following acronyms: polylactic acid (PLA), thermoplastic starch (TPS), polyethylene terephthalate (Bio-PET), high-density polyethylene (Bio-HDPE), polyvinylchloride (Bio-PVC), polytrimethyl terephthalate (Bio-PTT), polypropylene (Bio-PP), and polyurethane (Bio-PUR). See Appendix A, supplemental data 17 for full figure data and PHB from biogas data.

In general, we find that a primary driver in environmental impacts of these materials is the type of feedstock used. For example, when using a mass-allocation approach, Bio-PET, Bio-HDPE, Bio-PVC and Bio-PTT have lower GWP when they are produced from 1st generation feedstocks, such as sugarcane sugar or corn, rather than 2nd generation feedstocks, such as corn stover or wheat straw due to lower agricultural requirements (e.g. higher crop yield), and the lack of need for pretreatment steps, thereby reducing impacts associated with enzyme and chemical production. It is important to note that only direct land-use change is incorporated in this study, and therefore GHG emissions associated with indirect land-use change could have a significant impact on the results and serves as an important area for future research.

3.1.1 Agricultural

Fertilizer production and use is one of the largest contributors to emissions of 2nd generation feedstocks, such as corn stover and wheat straw. For example, 17% of CO₂ emissions associated with PLA production from corn stover came from the production of ammonia for corn cultivation. Industrial ammonia production emits more CO₂ than any other chemical-producing process [118] resulting from extremely high energy demand and the use of hydrogen via the Haber-Bosch process. Even when high-temperature and high-pressure process requirements are met with renewable energy (as it is modeled here), the production of hydrogen required for the reaction is currently made from natural gas, coal, or oil, via a process that accounts for more than half of the CO₂ emissions from ammonia production. To minimize these emissions, hydrogen could be produced from renewable resources via electrolysis [119] and alternatives to the Haber-Bosch process that may improve efficiency could be investigated [120].

In addition to the production of ammonia, its application contributes significantly to N₂O emissions due to biological processes such as nitrification and denitrification. In 2005, only 17% of nitrogen produced for agriculture remained in the final product [121,122]. As a result, for bio-based plastics with high agricultural feedstock inputs, such as Bio-PET and Bio-HDPE (7.5 and 4.04 kg corn stover, respectively), N₂O emissions from corn stover cultivation led to substantial GHG emissions - roughly 34 and 29% of the total mass-allocated GWP for these plastics respectively. The same relative contributions hold true for Bio-PVC from corn stover and Bio-PTT from corn/corn stover, with roughly 27% and 35% of GWP coming from N₂O field emissions respectively. To reduce the magnitude of nitrogen emissions from fertilizers, various agricultural process improvements could be implemented such as: (1) drainage systems to help maintain optimal moisture content and reduce denitrification of ammonia; (2) inserting ammonia-based fertilizer deeper into the soil to reduce ammonia volatilization; and (3) utilizing a need-based approach for fertilizer application to reduce excess nitrogen runoff [123].

3.1.2. Processing/conversion

Enzyme production is a significant source of processing and conversion emissions for bio-based plastics made from lignocellulosic materials. Enzymes are required for the enzymatic hydrolysis of lignocellulosic feedstocks, which is an energy and emissions intensive process. Here we modeled this enzyme production based on the ecoinvent LCI for potato starch-derived enzymes. A notable fraction of the emissions from this enzyme production process, once energy-emissions are eliminated, are attributable to the agricultural processing of potatoes. In addition to reducing fertilizer use, another potential process improvement would be to investigate the use of 2nd and

3rd generation feedstocks for enzyme production [124]. Furthermore, reducing enzyme loading while maintaining high yields could lower energy requirements, as well as make the process more economically desirable [125]. It has been suggested that such loading could be lowered by 50% [126]. Studies have also investigated an alternative to enzymatic hydrolysis – a one-step chemical hydrolysis process – that can help reduce GHG emissions by 54% compared to enzymatic hydrolysis [108].

Beyond enzymes, chemicals required to convert biomass feedstocks to bio-based plastics can contribute to cradle-to-gate GHG emissions. For example, triethylamine and magnesium hydroxide ($Mg(OH)_2$), both required for the neutralization of lactic acid in the production of PLA from sugarcane bagasse, contribute 22% to cradle-to-gate mass-allocated GWP. Similarly, the extraction of PHB from microbial cells, regardless of the initial feedstock, is an energy and chemical-intensive process; we note again, different methods [59] could be used for extraction and we model a solvent-based method here due to wide use. It is likely that the process efficiency for PHB extraction will improve once production reaches commercial scale [127]. Moving forward, utilizing less carbon-intensive chemicals, such as NaOH instead of chloroform, could also reduce emissions [128].

For bio-based plastics that are partially fossil-based such as Bio-PUR or TPS, petrochemical production processes can amount to 84-97% of the production-related emissions. This factor is well exemplified by flexible and rigid Bio-PUR foam, whose LCIs differ in the ratio of biomass to petroleum feedstocks and the type of petroleum feedstock used (toluene diisocyanate (TDI) vs. methylene diphenyl diisocyanate (MDI)). Driven by its higher biomass to petroleum feedstock

ratio, the cradle-to-gate mass-allocated GWP for the flexible Bio-PUR are over 100% lower than rigid foam. However, even with increased biomass content, the majority (55%) of GWP for flexible PUR foam comes from the production of diethanolamine, a chemical required to produce polyol from vegetable oil, whereas for rigid PUR foam, the majority (78%) of the GWP comes from the production of MDI. Despite the use of renewable energy, both plastics result in significant emissions due to the petroleum feedstocks required for production. While this work focuses on GHG fluxes, there are also human health concerns that should be addressed, with MDI and TDI resulting in increased asthma risk for occupational workers in foam manufacturing [129]. Therefore, deriving less harmful, bio-based alternatives to TDI, MDI and DEA is a necessary area for study. Bio-based non-isocyanate urethanes derived from plant oil have been produced on a lab-scale, but they still require an in-depth analysis of their potential environmental impacts [130].

Given that there are no upstream environmental impacts attributed to the feedstock, used cooking oil, for Bio-PP production, the majority (93%) of mass-allocated GWP comes from the hydrotreatment process of oil. This process requires hydrogen which is produced via natural gas reformation. To reduce production related emissions, the production of hydrogen via electrolysis using renewable energy could be explored. In addition to using waste oil as a feedstock, GHG-negative Bio-PP could be made by synthesizing methanol from atmospheric CO₂ and H₂, again, assuming all energy demands and hydrogen production are satisfied by renewables [131].

In addition to the environmental impacts of agricultural and chemical production processing, a significant source of CO₂ emissions come from inefficiencies in the bio-based plastic production

processes. For example, 5.26 kg of CH₄ from landfill biogas are required to produce 1 kg of PHB due to inefficiencies associated with PHB extraction from microbial cells. However, an optimized system for PHB production could reduce feedstock inputs to <3 kg of CH₄ [59] and simultaneously utilize the CO₂ emissions from biogas as a feedstock for plastic production, to reduce overall GHG emissions and costs associated with PHB production. Similarly, the production of Bio-PET and Bio-HDPE requires 7.5 and 4.04 kg corn stover, corresponding to 3.3 and 1.8 kg of carbon, but only 20 and 48% of the carbon ends up in the final product, respectively. Therefore, process improvements for these materials include increasing the efficiency of TPA and ethanol production pathways to reduce losses and minimize primary feedstock inputs. A more efficient production route for TPA via direct fermentation of sugars could reduce the loss of carbon as well as minimize capital and operating costs [110]. Engineering bio-based plastics can capitalize on such methods.

3.2 Role of methodological assumptions

When determining the environmental impact of an agricultural by-product, such as corn stover or wheat straw, the upstream impacts (such as emissions associated with land-use, fertilizer production and application, and fuel consumed by agricultural machinery) need to be applied to both the main crop and the by-product. ISO 14040 recommends applying system expansion to avoid allocation, thereby encompassing the impacts associated with all of the products and byproducts within a system [65]. However, applying system expansion is data intensive and requires making assumptions on the behavior of the system, which can lead to high uncertainty. Alternatively, the impacts of these upstream processes can be divided up (or allocated) based on economic or physical relationships or can be entirely attributed to one “main” product. Three

common allocation methods are examined herein: (1) mass allocation, utilizing physical relationships to allocate impacts; (2) economic allocation, addressing economic value of products, which can drive production rates and market behavior; and (3) no allocation, which attributes all impacts to one product and is commonly used in LCAs examining 2nd and 3rd generation feedstocks [60,132,133]. Economic allocation provides the benefit of potentially reflecting real-world resource consumption patterns based on market values of materials. However, economic values vary greatly over time and across different regions, leading to high variability among results. Mass allocation provides the benefit of remaining consistent by utilizing a physical relationship to allocate impacts. However, applying mass-allocation may result in attributing a large amount of environmental impacts to inevitable waste streams and simultaneously undervaluing the impacts of the main product.

Our findings show that CDR production pathways are possible depending on the allocation method used. **Figure 5** shows the impact of varying allocation methods on the cradle-to-gate GWP of the bio-based plastics considered in this work. Our findings show that mass allocation results in the highest apparent GWP for all materials made from 2nd generation feedstocks (e.g., from corn stover or wheat straw), with economic allocation and no allocation resulting in 137% and 170% lower GWP on average. These findings are expected given that the mass allocation factor for 2nd generation crops is typically higher than the economic allocation factor [134]. No allocation results in the highest impact for bio-based plastics from 1st generation feedstocks (e.g., from corn or rapeseed oil). On average, no allocation and economic allocation resulted in 69% and 28% higher GWP compared to mass allocation for 1st generation bio-based plastics. These findings are expected given that under no allocation, all upstream impacts from crop cultivation

are attributed to the 1st generation feedstock. The key exceptions to these trends are for the bio-based plastics made from sugarcane molasses. Sugarcane molasses, a second generation feedstock, has a higher factor for economic allocation than for mass allocation (see Table 1) because it is typically sent to distilleries for ethanol production [135]. However, it is not considered the main product of sugarcane, which is sugar, therefore no allocation results in the lowest GWP.

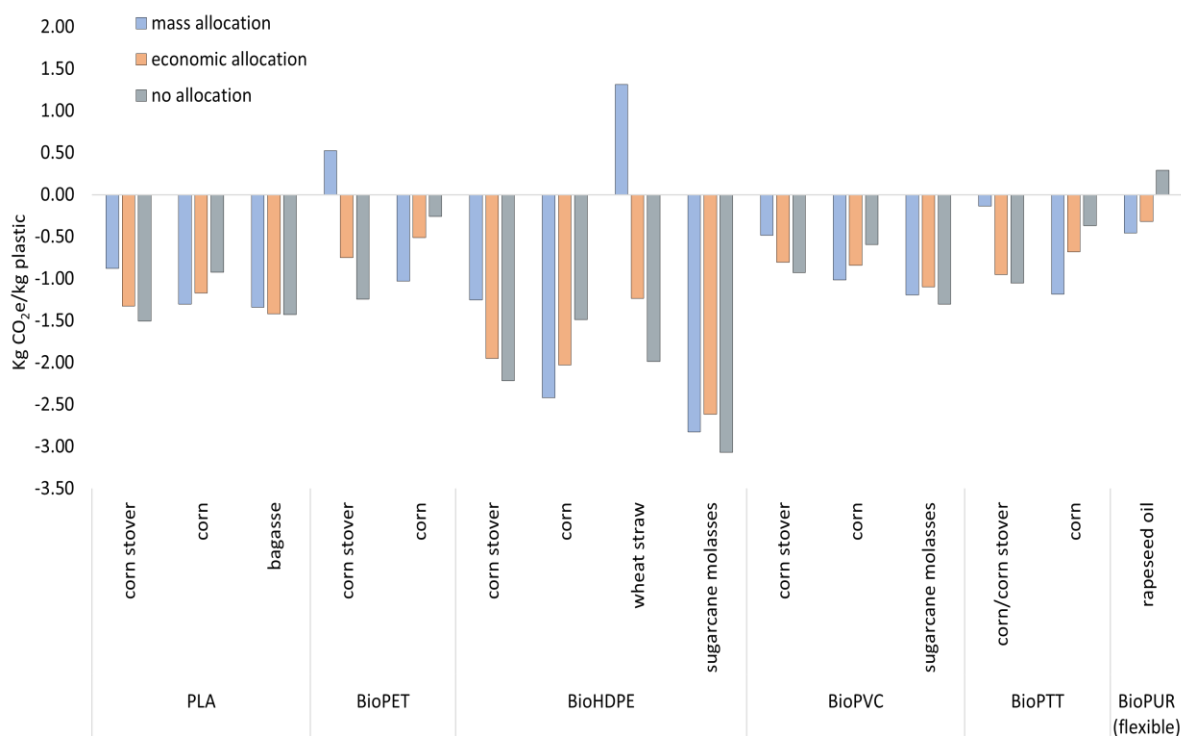


Figure 5 Cradle-to-gate GWP of bio-based plastics produced from various feedstocks, using 100% renewable energy and allocating impacts based on mass (light blue), economic (orange), no allocation (gray). CO₂e was calculated using GWP factors for CO₂, CH₄ (28) and N₂O (273) emissions. Note the following acronyms: polylactic acid (PLA), polyethylene terephthalate (Bio-PET), high-density polyethylene (Bio-HDPE), polyvinylchloride (Bio-PVC), polytrimethyl terephthalate (Bio-PTT), and polyurethane (Bio-PUR). See Appendix A, Supplemental data 18 for full figure data. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

How biogenic carbon is addressed in the GHG fluxes for plastics production affects not only the GHG emissions profile for the plastic, but also the extent to which selecting a different allocation method alters the net impact. Biogenic carbon accounting is a common source of variability among bio-based plastic LCA studies [125,134]. In this study, biogenic carbon credit is applied based on the carbon content of the bio-based plastic, meaning that the benefits of removal of atmospheric CO₂ is the same regardless of the allocation method. We selected this method of accounting as it reflects the bound carbon in the material. However, other authors have used other methods. For example, Luo *et al.* [134] allocated biogenic carbon the same way that other emissions, such as N₂O, are allocated. For an assumption like Luo *et al.*'s, mass allocation correlates to a higher biogenic carbon credit than economic allocation for 2nd generation feedstocks. This difference in methodology results in the opposite trend than what is observed herein, with mass allocation resulting in lower GHG emissions compared to economic allocation for bio-based plastics from 2nd generation crops. This notable difference in results highlights the need for standardization among allocation methods in LCAs, specifically for 2nd and 3rd generation bio-based materials.

The sensitivity of GHG emissions (or magnitude of net-uptake) to the allocation methodology used depends on the type of bio-based plastic. For plastics where the biomass resource used contributes low amounts to GHG emissions, there is lower variation resulting from selecting a different allocation method. For plastics where a substantial amount of the GHG emissions profile is driven by the biomass resource, greater fluctuation in findings can occur by applying a different allocation method. For example, given that the feedstock inputs are much higher for Bio-PET than they are for PLA, the impact of allocation methods are much more significant.

4. Discussion

The goal of this study is to present LCI data for GHG-negative bio-based plastic production pathways from 2nd and 3rd generation feedstocks. While GHG-negative production pathways were identified, it is important to address some of the barriers and limitations of such methods. For example, although the electricity and energy requirements are modeled as using renewable resources, there are some scenarios where transitioning to renewable energy could be challenging given the high-temperature or high-pressure requirements of a given process. The Haber-Bosch process for ammonia production requires temperature and pressures above 700°C and 200 bar [115]. Although some renewable energy technologies (such as solar thermal energy), are technically capable of satisfying high temperature requirements, the capacity of such technologies are not yet sufficient to meet the energy demands of the plastic industry. The petrochemical industry consumes 30% of total final industrial energy use globally [29], whereas wind and solar energy currently only make up 2.7% of total global energy demand [136]. Similarly, despite the growth in installed bioenergy capacity over recent years, biomass energy only contributes ~9% to total global energy demand [136]. Therefore, while the environmental hotspots discussed herein are still relevant, it is important to note that decarbonizing the plastic industry remains a challenge. Proposed solutions to the environmental hotspots addressed herein outside of energy demand include the use of renewable hydrogen, decreased fertilizer demand, isocyanate-free PUR production, and alternative methods for enzymatic hydrolysis. It is crucial to acknowledge that implementing these solutions in the near future may face challenges such as high cost, insufficient infrastructure for scaling, and absence of established value chains. For example, despite the technological maturity of green hydrogen production, 99% of hydrogen is still produced from fossil fuels largely due to cost barriers [137].

Another potential limitation to the solutions proposed herein is the availability of 2nd and 3rd generation feedstocks. While these biomass residues provide a source for plastic production without limiting food availability, the total quantity produced may not be sufficient to meet global plastic demand. In this work, we present LCIs for bio-based plastics capable of replacing 80% of current fossil-based plastic. This assumption is based on their technical performance, rather than on resource availability. To reach the 80% substitution rate referenced herein, alternative production routes such as algae or CO₂-based plastics, may need to be developed. However, if closed-loop end-of-life strategies are implemented for bio-based plastics (such as chemical recycling), annual biomass demand for bio-based plastic production would only amount to 23% of the projected untapped biomass resources (such as lignocellulose and food waste) estimated to become available due to improved farming [42].

While this study focused on cradle-to-gate impacts of bio-based plastic production, end-of-life impacts remain significant. These end-of-life impacts may be notable for biodegradable bio-based plastics (PLA, PHA, TPS), since anaerobic biodegradation of these materials at end-of-life can release methane [37]. Therefore, it is important to note that achieving cradle-to-grave net-negative emissions for bio-based plastics may only be feasible under certain end-of-life conditions such as recycling, anaerobic digestion or composting. Another potential limitation to this study is that some of the LCI data that is used is region-specific (for example, corn and corn stover production are based on US average values). Grabowski *et al.* reviewed currently available datasets for bio-based plastic feedstocks, and found that 60% of the available datasets were based on two regions: North America and Europe [138]. They also found that the data for

most crops were out-of-date. In this study, this temporal data gap is partially addressed by using updated crop yield statistics, but it remains a concern for other inputs such as fertilizer and harvesting methods which can vary greatly by region as well as over time. Furthermore, given the attributional approach of this study, the impacts of alternative scenarios and/or interconnected processes are not captured. For example, we model sugarcane bagasse as a feedstock for bio-based plastic production, when it is typically used as an energy-source. Future work could apply system expansion in such cases to capture the impacts of such alternative scenarios.

Countless studies have discussed the necessity to decarbonize the petrochemical industry, and the global theoretical potential to make the petrochemical industry net-zero has been explored. However, pathways to create net-zero or net-uptake systems need to be systematically quantified and assessed. By creating a harmonized method for systematically quantifying GHG fluxes for bio-based plastics, this work shows the necessary technological advancements to eliminate GHG emissions from the production process of plastics. As noted, the plastics examined in this work have the technical potential to substitute roughly 80% of the current petroleum-plastic market. Given that depending on the allocation method considered, GHG-negative plastic production methods were identified, findings can be used to inform stakeholders along the plastic supply chain of mechanisms to drive GHG-negative plastics. However, this shift towards bio-based plastics would not be an economically viable emissions mitigation strategy if only 1st generation crops are used due to land-use change impacts and competition with food [34]. By presenting production pathways for bio-based plastics from non-edible feedstocks, new markets for agricultural byproducts can be driven [139]. Such alteration would not only mitigate reliance on

petroleum resources for consumer products, but also potentially mitigate inefficient utilization of, and create new markets for, the roughly 1 billion tonnes of agricultural and food waste generated globally each year [116]. Such a shift in resource use could contribute to the reduction of resource transportation, the mitigation of harmful emissions from petroleum refinement [140], and the limitation of insecurities associated with supply chain dynamics if implemented properly.

5. Conclusion

In this study, GHG-negative production pathways were identified for nine bio-based plastics. Harmonized LCIs were derived for these plastics to facilitate comparison, analysis, and improved production. This level of transparency will not only support scientific advancements, but also help eliminate the black box that exists in many petrochemical production methods. Together, the plastics explored are technically capable of substituting roughly 80% of current fossil-based plastic demand, suggesting a potential for the plastic market to become a carbon sink rather than a significant carbon source. Furthermore, all of the bio-based plastic production pathways examined herein at least partially utilize 2nd or 3rd generation feedstocks, which reduce competition with food and land-use change impacts - two major problems typically associated with bio-based plastic production.

Applying the LCIs synthesized in this work, our analysis of GHG emissions hotspots highlighted the need for various process improvements outside of decarbonizing energy and electricity demands, including:

- reducing ammonia-based fertilizer use
- engineering greener methods for H₂ production such as electrolysis via renewable energy

- using bio-based, isocyanate-free PUR production pathways
- using 2nd-generation feedstocks for enzyme production
- determining alternatives to enzymatic hydrolysis such as one-step chemical-hydrolysis
- engineering bio-based alternatives to typical fossil-based TPS blends
- improving process efficiencies in TPA and ethanol production pathways to reduce CO₂ emissions from biomass loss

Our work also considers the sensitivity of modeling outcomes to allocation methods. Generally, mass allocation of 2nd generation feedstocks resulted in the highest GWP, while economic or no allocation resulted in the highest GWP for 1st generation feedstocks. However, these results can shift due to changes in methodology such as biogenic carbon accounting (e.g., either applying biogenic carbon credits based on the carbon content of the final product or based on an allocation factor). Therefore, there is a need for standardization and clear guidelines regarding biogenic carbon accounting and allocation methods as they apply to bio-based materials.

When considering drastic changes in production processes, such as shifting from fossil-based to bio-based plastics, it is important to reduce burden shifting or reducing one environmental impact category at the expense of another. Therefore, future work should aim to understand the environmental and human health impacts outside of GHG emissions of the bio-based plastic production pathways presented herein, such as particulate matter emissions and eutrophication impacts from fertilizer use [141], human health burdens from the combustion and conversion of fuels for energy generation [142,143], and increased water demand associated with bio-based feedstocks [34]. In addition, investigating the consequential impacts of large-scale bio-based

plastic production, such as indirect land-use change, and shifts in biomass markets, should be further analyzed. Data gaps that exist in plastic production inventories, such as the use of additives should be investigated to better understand the impact of these materials on the environment, and continued integration of updated life cycle inventory data, particularly when geographically and temporally relevant, should be studied. Finally, to achieve net-zero plastics, the end-of-life impacts must also be considered. Therefore, determining the impact of waste management strategies on the GHG-negative potential of bio-based plastics is critical.

Chapter 3. End-of-life impacts of bio-based plastics

Authors note: This chapter is from the publication “A review of bioplastics at end-of-life: Linking experimental biodegradation studies and life cycle impact assessments” published in *Resources, Conservation, and Recycling* (2022) 106236. <https://doi.org/10.1016/j.resconrec.2022.106236>.

Abstract

This review examines cradle-to-grave life cycle assessments (LCAs) and biodegradation studies of common biodegradable, bio-based plastics. Fueled by a growing single-use consumer base, the rate at which plastics are produced and disposed of is outpacing most other human-made materials, leading to substantial environmental impacts. Plastics from bio-based feedstocks are a commonly discussed method to mitigate impacts of fossil-based plastic production. However, there is still a limited understanding of the best practices for waste management of these plastics. Here we review the end-of-life (EoL) assumptions for bio-based plastic LCA studies and compare these to experimental findings to identify research gaps and highlight sources of uncertainty. The majority of existing LCA literature, including 17 out of 22 studies reviewed herein, focus on the environmental impacts from three key biodegradable, bio-based plastics: polylactic acid, polyhydroxyalkanoates, and thermoplastic starch. However, these bio-based plastics are projected to account for only 29% of the future plastic consumption based on their current technical feasibility. Further, within these LCA studies, there remain limited modeling efforts for anaerobic digestion as an EoL option; yet, this is one of the predominant disposal pathways studied in the experimental literature. Due to limited data for the behavior of bioplastics at EoL, LCA studies contain assumptions that lead to high levels of variability and uncertainty in environmental impact results, with many modeling assumptions and by-product

applications differing significantly from the current waste management system. Findings of this review also highlight areas of future research, such as mechanisms to leverage the potential circularity of these bio-based plastics.

1. Introduction

The consumption of single-use plastics has been on the rise for years due to their low cost, light-weight, and durability [144]. Plastics have allowed for many technological advances such as high strength-to-weight ratio construction and automotive materials, as well as highly resistant food packaging [145]. However, conventional plastics are made from petroleum feedstock. This feedstock coupled with current manufacturing methods leads to high environmental impacts from plastics production [9]: production of plastics is responsible for ~4% of global CO₂ emissions [9] and significant methane emissions due to supply chain leakages, which are often un-accounted for [146]. While recycling plastics can improve resource circularity and lower certain environmental impacts from production [147], the current recycling rate for plastics remains low: less than 10% in the U.S. [148]. Globally, approximately 80% of all plastics discarded between 1950-2015 ended up in landfills or in the natural environment [10]. The breakdown of plastics in the environment leads to micro and nano-plastic releases [149]. These particles can negatively impact water and soil quality, as well as human health [150,151].

The emissions from producing plastics could be partially alleviated through the substitution of feedstock resources used, namely with biogenic resources. Common biogenic feedstocks for plastics include sugarcane, corn, and cassava [152]. Manufacturing plastics using biogenic resources could lead to a reduction in greenhouse gas (GHG) emissions by up to 225% compared

to conventional plastics [83,153–156]. Further, some have argued these plastics could be engineered to act as carbon sinks due to the uptake of CO₂ during feedstock cultivation, resulting in cradle-to-gate emissions of as much as -6.06 to -1.7 kg CO₂-eq/kg polymer [59,99,157].

At end-of-life (EoL), plastics capable of biodegrading have been proposed as a means to alleviate environmental burdens. Biodegradation is generally defined as the breakdown of a material by microorganisms resulting in environmentally benign substances such as CO₂, water and biomass [158]. The three-step process begins with what is sometimes referred to as biodeterioration, also known as the “lag phase”, where microorganisms grow inside or on the material and cause changes to the polymer’s physical, chemical and mechanical properties [159]. Polymers are then broken down by the microorganisms into oligomers and monomers in a process commonly called biofragmentation, which is also considered the growth phase for microorganisms [159]. Finally, microorganisms use the nutrients supplied by the degradation of polymers to generate energy, CO₂, water and new biomass [159].

Plastics from biogenic feedstock materials or biodegradable plastics are often called “bioplastics”. Bioplastics is an umbrella term that can be split up into three main groups: (1) bio-based (i.e., from biogenic feedstock) biodegradable, (2) bio-based non-biodegradable, and (3) fossil-based biodegradable. Bio-based non-biodegradable plastics, such as bio-based polyethylene terephthalate (bio-PET) and bio-based polyethylene (bio-PE), are sometimes called “drop-in” plastics because they are chemically and structurally identical to their fossil-based counterparts despite being made from biogenic resources. This review focuses on the most common bio-based and biodegradable plastics: polylactic acid (PLA), polyhydroxyalkanoates

(PHAs), and thermoplastic starch (TPS). These three classes of bioplastics made up roughly 40% of the bioplastic market in 2020 [160]. Applications for these bioplastics include food packaging, thin films, medical implants, bags, automotive parts, and use in construction [152].

Although bioplastics currently make up only 1% of the global plastics market, their market share is expected to grow 35% by 2025 [161]. Further, it is projected that bioplastics have the technical ability to substitute 90% of current plastic usage, though only 35% can be satisfied with biodegradable bioplastics [18]. Unlike conventional plastics, total life-cycle emissions of bioplastics depend heavily on the EoL pathway due to the emissions associated with biodegradation [147,155,162,163]. Reports have suggested that the EoL of fossil-based plastics accounts for less than 10% the life-cycle GHG emissions[9]. Conversely, for bioplastics that fully degrade in landfills, the emissions from EoL can be as high as 80% of the life-cycle GHGs when including biogenic emissions (i.e., not assuming biogenic emissions are net-neutral) [164]. Therefore, given anticipated demand for bioplastics, it is crucial that the environmental impacts and appropriate waste management of these bioplastics are realized.

This review analyzes the potential impacts, sources of uncertainty, and research gaps for various EoL options for PLA, PHAs and TPS. First, an overview of the different EoL options and the current waste management strategies for plastics is presented. Then life cycle assessment (LCA) and biodegradation studies of bio-based plastics in compost, anaerobic digestion (AD), and landfills are discussed. The factors affecting the rate of and extent of biodegradation as well as the methodological assumptions and results from LCA studies are analyzed in order to highlight sources of uncertainty and draw comparisons.

2. Methods

The literature for this review was collected through a systematic search methodology (see Appendix A). A total of 61 papers were identified; 22 LCA papers that include EoL in the scope, and 39 experimental biodegradation papers that examined PLA, TPS, or PHAs in AD, compost or landfill conditions. Given the limited use of pure starch in the bioplastic industry, TPS blends such as the commercial Mater-Bi from Novamont were included in this review (see Appendix A, S5 for details regarding the TPS blends examined in each biodegradation study). The complete list of LCA and biodegradation papers as well as relevant values extracted are summarized in Appendix A (S1-S7). For the comparison of biodegradation and LCA studies, the LCA literature was narrowed further to only include papers that presented GHG values associated with individual processes (as opposed to a single value for the full life cycle). Therefore, half of the studies, which did not report extractable GHG values, were excluded from the comparative analysis. This methodology was used to search two databases, Google Scholar and Web of Science, for literature.

3. EoL options for bio-based plastics

In addition to traditional plastic EoL pathways (i.e., recycling, incineration, and landfill), biodegradable plastics can also be treated as organic waste and discarded in compost or AD systems. Diverting organic waste from landfills lessens the space required for municipal solid waste (MSW) and allows for the energy and nutrients of materials to be harnessed rather than wasted. These harnessed resources can offset other products, such as fertilizers and energy resources, supporting a circular economy. Despite these advantages of alternative EoL pathways, the current waste management system for plastics is not designed to make use of biodegradable

materials. With the exception of complete recycling, each of these EoL pathways are all anticipated to result in a certain degree of GHG emissions for bioplastics. In 2015, approximately 58% of global plastic disposals were in landfills, 24% were incinerated, and 18% were recycled [9]. The recycling rate for plastics is even lower for the U.S., which has remained around 9% since 2012 [10]. The anaerobic biodegradation of biodegradable plastics in landfills results in methane emissions, which means that, depending on the landfill gas capture technology available, this dependence on landfilling could have harmful ramifications when transitioning to biodegradable plastics. Therefore, it is important that the impacts of alternative waste management strategies such as composting and AD as well as the recyclability of bio-based plastics is considered to inform appropriate waste management. In this section, we summarize the key EoL pathways for bio-based plastics.

3.1 Recycling

3.1.1 Thermomechanical recycling

Conventional recycling relies on thermo-mechanical processes and would typically be anticipated as a favorable EoL pathway in terms of GHG emissions and resource consumption; therefore, it is critical to estimate the recyclability of bio-based plastics. An important first step of the thermomechanical recycling process is the separation of plastics since they are often mixed with non-recyclable materials. Given that the separation operations are not perfect, any remaining mixed plastic waste that is not separated out gets sent to an incinerator or landfill. The sorted plastic wastes of the same type are then milled, washed and dried. Plastic recyclates can either be used directly or formed back into granulates prior to secondary use. PLA, the most abundant bio-based plastic on the market, can be recycled using the same machinery as

traditional fossil-based plastics [164]. However, the number of extrusion cycles that the material can withstand is largely unknown. Zenkiewicz *et al.* found that PLA can be recycled 10 times before losing just over 5% of its original tensile strength [165]; however, use phases in between cycles were not considered. Other studies have observed significant losses in mechanical properties and molecular weight of PLA from multiple processing cycles [166]; yet certain additives, such as chain extenders, can be added to restore the molecular weight and viscosity of PLA [166]. There are few studies regarding the recyclability of other neat biopolymers such as PHB due to their limited use. However, some studies have found that PHB co-polymers such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), have the ability to be recycled up to 5 times without having a significant impact on mechanical properties [167].

Traditional thermomechanical recycling of these materials has an additional barrier: contamination of fossil-based recycling systems. Mixing just 10 wt.% biodegradable plastic with fossil-based plastics has been shown to greatly lower the mechanical properties of recycled fossil-based plastics [168]. Further, as little as 0.1 wt.% of PLA can cause substantial discoloration of recycled PET [169]. It has been suggested that consumers are prone to using similar disposal methods for bio-based plastics as fossil-based plastics; for example, Dilkes-Hoffman *et al.* found that 62% of Australian survey respondents said that they would dispose of bio-based biodegradable plastics in the recycling bin [170]. Potential solutions to this problem include the use of near-infrared spectroscopy (NIS), which can sort plastics with over 97% accuracy [171]. Other potential separation technologies for biodegradable plastics include density separation, air separation, and dye tracers [172]. However, the multiple layers containing different materials and additives in plastic products could still pose a challenge: for example, a

study conducted in the UK found that 21-40% (by weight) of plastic in a typical grocery cart could not be recycled, even if it were separated, washed and sent to recycling [173].

3.1.2 Alternative recycling pathways

Chemical and biological recycling could overcome the limitations and difficulties of thermomechanical recycling. Both chemical and biological recycling support a depolymerization process in which the plastics are broken down to their monomer backbones. These monomers can then be used to form new plastics, which can have identical mechanical properties to their virgin material. Alternatively, plastics can be broken down to oligomers, which can be used as building blocks for alternative polymers.

In chemical recycling, depolymerization is performed through the use of heat and/or chemicals. Chemical recycling methods with the highest technology-readiness level include pyrolysis, gasification, and solution-based catalytic depolymerization such as alcoholysis or hydrolysis [174,175]. Pyrolysis and gasification can both break down mixtures of plastics into intermediate products in the presence of heat, with pyrolysis occurring in the absence of oxygen and gasification utilizing steam or air. Unlike other chemical recycling methods, pyrolysis and gasification do not require homogenous plastic waste streams [176]. In addition to the production of monomers which can be made into material products, these chemical recycling processes result in useful byproducts such as H₂, coke, and hydrocarbons [175]. Recent studies have found that alcoholysis of PLA using a dual catalyst system can result in over 97% formation of alkyl lactate. Alkyl lactate can then be used to generate lactide for PLA production [177].

Biological recycling processes differ from chemical recycling in that they utilize microbial organisms, rather than chemicals, to undergo the depolymerization process. These microorganisms derive enzymes (such as amylases, lipases, and carbohydrases) to produce fuels, biopesticides, and oils [176,178]. This method has promising results; for example, Tournier *et al.* found a hydrolase enzyme capable of converting 90% of PET back into its monomer in just 10 hours [179]. This form of biological recycling is also known as “up-cycling” due to its ability to produce valuable monomers as well as other polymers and chemicals as opposed to traditional biological degradation or “organic recycling” which down-cycles biodegradable plastics into biogas and compost. Although biological recycling is a viable EoL method for PHAs and TPS, the rapid enzymatic degradation into CO₂ makes it hard to obtain useful intermediates [180,181]

3.2 Incineration and energy recovery

After landfills, the second most popular disposal route for plastics globally is incineration and energy recovery [9]. Controlled combustion can be used to harness and convert the calorific value of wastes into useful heat or used for electricity generation, and simultaneously reduce the volume of MSW [182]. This method of resource recovery from fossil-based plastics is common in Europe, where in 2018 roughly 40% of plastic waste was sent to municipal solid waste incineration (MSWI), meaning the mixed plastic was incinerated rather than landfilled [145]. Bio-based plastics can be incorporated into such conventional plastic waste incineration facilities due to their high calorific value and ready flammability [183,184]. Although starch-based plastics have a slightly lower gross calorific value than coal, it is still comparable to that of wood and therefore a viable source of energy [185]. An added benefit of incinerating bio-based plastic waste is that unlike with fossil-based plastics, the CO₂ that is emitted can be thought of as net-

neutral. However, given the biodegradability of these materials, incineration can be considered a waste of valuable nutrients that could otherwise be utilized again as fertilizer. Further, given that the incineration of fossil-based plastics results in high emissions, the GHG neutrality benefits of incineration wouldn't be realized unless the plastic market shifts entirely to bio-based resources. Despite the popularity of incineration as a disposal route for plastics, there are a number of health concerns associated with the process. Among the largest of these concerns is the release of toxins [186]. Health issues associated with emissions from incineration can cause birth defects, non-cancerous disease, and site-specific tumors [187]. However, there are various mechanisms and controls that can be used to manage emissions, which are supported by enforcement of environmental regulations (e.g. Toxic Substances Control Act). For example, modern incinerators employ high temperatures (850°C) to expose pollutants to thermal cracking [188].

3.3 Compost

During composting, organic matter is broken down by a group of microorganisms, producing CO₂ and humus. The standards for what classifies as a compostable plastic have varying definitions, but they often rely on either a mass loss over a defined time period (e.g., EN 13432 [189]) or a combination of material loss and the formation of CO₂, water, biomass, and inorganic compounds (e.g., ASTM D6400 [190]). The extent of biodegradation of a polymer is sometimes calculated using the difference between the amount of CO₂ produced and the theoretical amount of CO₂ produced. The theoretical CO₂ (Th_{CO₂}) resulting from the aerobic biodegradation of biodegradable plastics can be calculated using the general equation seen in Eq 1, where Th_{CO₂} is in units of g CO₂/g polymer, C_{tot} is the ratio of organic carbon (g) to the molar mass of polymer, and 44 and 12 refer to the molecular mass of CO₂ and atomic mass of C respectively.

$$Th_{CO_2} = C_{tot} * \frac{44}{12} \quad (1)$$

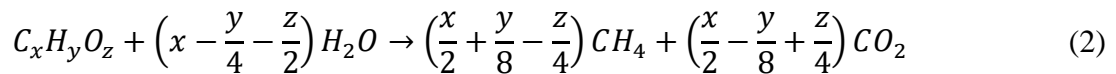
Industrial composting typically takes place at warm temperatures (60-70 °C) and with high moisture contents of about 60% [191]. The availability of water is important for aerobic biodegradation as it acts as a distribution network for microorganisms [192]. In addition, the compost composition and physiochemical properties also play an important role as compost supplies the nutrients necessary for the growth of microbes. The ideal carbon to nitrogen (C:N) ratio for compost can be anywhere between 14 and 43 [192]. A C:N ratio that is too high would slow down the biodegradation process since N is the limiting reagent whereas C:N ratio that is too low would result in excess N being converted to NH₃ [192].

Although bio-based plastics such as PLA, TPS and PHB have been certified as compostable on the lab-scale, research is still being done to examine their potential impacts on resulting compost quality. For example, Bandini *et al.* simulated real-life industrial compost conditions for PLA water bottles mixed with the organic fraction of municipal solid waste (OFMSW) and found that the lactic acid from PLA degradation reduced the pH of the resulting compost, negatively impacting seed germination [193]. Regardless of this potential reduction in soil quality, composting is a common EoL pathway that is included in many LCA and biodegradation studies of bio-based plastics. However, it makes up a small portion of the waste management system globally. Organic material makes up roughly 56% of the total MSW generated globally, but only about 5% of the MSW is composted, with the majority going to landfills instead [194]. Not only does landfill disposal impact the GHGs formed during decomposition, but it also wastes a

resource that could be used to produce fertilizers, which in turn could help minimize the production of chemical fertilizers.

3.4 Anaerobic digestion

AD offers a method for energy and nutrient recovery of biodegradable plastics when mechanical recycling is not an option. In AD, organic matter is broken down in the absence of oxygen, which produces biogas and digestate. The four main steps in AD are hydrolysis, acidogenesis, acetogenesis, and methanogenesis, each of which requires a specific set of microorganisms [195]. The biogas resulting from these steps typically contains 50-60% methane and 25-50% CO₂ [196]. If captured, the methane from this biogas can be used as an energy source: depending on composition, one metric ton of biowaste can produce enough biogas to generate approximately 180 kWh of electricity [197]. As with biodegradation, there are standards to define an anaerobically digestible material (e.g., EN standard 13432 : 2000 states that a minimum of 50% of the material needs to be converted into biogas within 2 months [191]). Biodegradation experiments and LCA studies of bio-based plastics often refer to the theoretical methane potential of a material, which can be calculated stoichiometrically using the Buswell equation (Eq.2) [198]



For biodegradable plastics in particular, one of the biggest available markets is single-use plastics and food packaging [161]. Plastic food packaging is often difficult or even impossible to recycle due to contamination and is therefore typically incinerated or landfilled. However, AD can be a desirable waste management pathway if biodegradable plastics are disposed with food

waste, which would simplify the disposal process for consumers by eliminating the need for washing and sorting. In addition, most municipal sludge waste has a C:N ratio from 6:1 to 16:1, while the optimal C:N ratio for anaerobic digestion is in the range of 20:1 to 30:1 [199]. Therefore, due to the high carbon content of bio-based plastics, co-digesting them with traditional waste can increase the C:N ratio, thus resulting in a higher biomethane production. Previous reports have found that municipal wastewater resource recovery facilities saw an increase in electricity production from biomethane when utilizing biodegradable plastics as a co-digestate [200]. However, a C:N ratio that is too high could result in volatile fatty acid accumulation, which could inhibit biogas production [201]. The AD of bio-based plastics also offers the potential to create a circular life cycle: in anaerobic conditions, methanotrophic bacteria can consume the methane produced from the AD process to produce PHB, which can be decomposed again through AD [59]. By utilizing a waste resource, the cost of expensive carbon feedstocks, which typically accounts for 50% of PHB production costs, is avoided [202]. However, the current cost of PHB production from biogas is still relatively high due to the complex methods for extraction of PHB from microbial cells [203].

Despite the benefits of diverting waste from landfills by sending food waste and bio-based plastics to AD systems, fossil-based plastics could cause problematic contamination. Currently, waste sent to AD systems is sorted and pre-treated to remove contaminants, such as fossil-based plastics, to ensure a higher quality digestate. However, there is not a cheap and simplified method for distinguishing between fossil-based and bio-based plastics. Solutions for the issue of contamination could include enforcing a mandate for flexible food-packaging materials to be made of biodegradable bio-based plastics or better denoting between the two plastic types.

Further, current standards specify a minimum biodegradation on a timescale of 2 months, which does not align well with industry given that many anaerobic digesters have hydraulic retention times (HRTs) of less than 2 months. Altering the standards would result in less AD contamination but would make it harder for bio-based plastics such as PLA to qualify as anaerobically digestible. Therefore, future research should consider methods that could improve the rate of bio-based plastic biodegradation in AD systems to better match industry standards [191].

3.5 Landfill

The removal of resources through landfilling should be the last resort for final disposal of goods, yet it is the most common method of waste management for MSW: globally, approximately 61% of MSW is disposed of in a landfill [194]. This ineffective disposal method can lead to significant GHG emissions. Landfills are currently the third-largest source of human-generated methane emissions in the U.S., amounting to 15% of total methane emissions in 2018 [204]. Landfills also pose threats to human health, ecosystems, and soil and water quality. For example, leachate from landfills has been found to contain high levels of COD, BOD, and heavy metals, which can significantly contaminate surrounding soil and water quality as a result of percolation [205]. In addition, leachate can contain microorganisms such as Coliform, which can result in high levels of phytotoxicity when introduced to the soil [206]. Various studies have found that populations living near landfills experience health concerns including asthma and bronchitis [206].

For biogenic waste, such as bio-based plastics, the biodegradation process in landfills involves anywhere from 3 to 8 phases [207]. When biodegradable materials are placed in a landfill, any available oxygen is first depleted and converted into CO₂, followed by the reduction of carbohydrates into sugars (in the case of TPS) or the degradation into volatile fatty acids via hydrolysis (in the case of PLA and PHB) [208]. Acidogens then convert the sugars into organic acids which are further converted into acetic acid by acetogens [208]. During the final and longest stage of biodegradation, methanogens metabolize the substrates, producing methane and CO₂ which make up over 90% of landfill gas [208].

Because waste is continually added to the system, phases overlap and biodegradation mechanisms are coupled with thermal, mechanical, and hydraulic processes occurring at the same time, making determination of the quantity and rate of biogas production in landfills quite complex. Factors affecting biogas production in landfills include the amount and chemical composition of the waste, climate (e.g. humidity and temperature), and topography of the landfill [207]. Given the complexity of the landfill biodegradation process, recent studies have developed models for estimating real-time biogas generation in landfills using waste composition data and meteorological conditions [207]. Some of these models are capable of capturing a portion of the unpredictability of landfill behavior [208]. However, these models have only been used on a handful of case-studies and have yet to be implemented on an industrial scale.

Landfilling is currently among the most common disposal pathways for plastics [209]. If biodegradable plastics are disposed of similarly to current fossil-based plastics, mitigating landfill emissions using biogas capture technology will be critical. The potential uses for biogas expand beyond their use for bio-based plastic production; biogas from landfills can be used as a

substitute for natural gas. Unfortunately, due to the relatively high cost of biogas capture and purification, few landfills have the appropriate infrastructure: in the U.S. only 20% of landfills capture or flare biogas [210]. However, the implementation of biogas capture and utilization is expected to increase by 50% by 2040, according to the International Energy Association (IEA), due to the increasing number of policies aimed at cutting down GHG emissions [211]. Further, biogas capture efficiency is expected to increase, with newer technologies capable of capturing up to 94% of methane emissions [212].

4. Bio-based plastic biodegradation

4.1 Factors affecting biodegradation

4.1.1 Material properties

The complexity and sensitivity of the biodegradation process of bio-based plastics leads to variability in experimental results from the literature. The results from this literature review of biodegradation studies are not conclusive, with some plastics, such as PLA, having the potential to biodegrade anywhere from 0% to 100% in AD conditions. Further, PHAs, PLA and TPS were found to biodegrade differently from one another resulting from variations in their morphology, physiochemical characteristics, and biodegradation mechanisms. One source of variability among experimental literature is due to the differences in material properties between bio-based plastics (see Appendix A for basic material properties for PLA, PHB and TPS). In general, a higher molecular weight (MW), high crystallinity, or high glass transition temperature (T_g) can reduce biodegradability [213]. A higher MW generally corresponds to a longer chain length and a higher T_g . Together, these two factors make the polymer less flexible and increase the energy required to release consumable oligomers for microorganisms [214]. For these reasons, PLA is

found to biodegrade faster in its amorphous rather than crystalline form [215]. For example, Kolstad *et al.* observed no significant degradation of semi-crystalline PLA in landfill conditions, but saw up to 37% biodegradation of amorphous PLA [216]. Further, due to the long chain length and high MW of crystalline PLA, it must first be broken down via hydrolyzation at high temperatures before biodegradation can start [191]. Given that commercial PLA has a higher T_g than PHB, it is shown to biodegrade less easily. Shin *et al.* [217] observed negligible biodegradation of PLA while PHBV reached 85% biodegradation in 20 days in anaerobic sludge.

The biodegradability of bio-based plastics can also change as a result of the addition of copolymers or additives. Given that the characteristics of starch-based bioplastics are not suitable for a number of plastic applications with exposure to moisture, blending them with other materials can improve their mechanical performance, but may also affect their biodegradability [218]. For example, depending on the composition of TPS, the degree of biodegradation among studies ranged from 22-100% for compost and 20-80% for AD [219,220]. Although pure starch is sometimes used as a control material in biodegradation studies, it is important to note that, due to the variability in biodegradation behavior of TPS blends, cellulose was the common control material in the biodegradation studies examined herein. Further research still should be conducted to understand factors contributing to the typical plateau at around 80% biodegradation in AD conditions for starch. In addition to material blends, various additives may also have an impact on the rate of biodegradation. Zain *et al.* [221], found that the addition of citric and ascorbic acid to TPS increased the moisture resistivity (15 and 20%) but simultaneously inhibited the ability of microorganisms to degrade the material. Given the large variation among

results from this literature review, such data are summarized in **Table 2** to highlight general trends.

Table 2 Summary of literature regarding the biodegradation behavior of bio-based plastics in different end-of-life (EoL) streams.

EoL Pathway	Material	Biodegradation Rate (%/day ⁻¹)*	%Biodegradation range (avg)	Lag Phase (days)	Growth Phase (days)	Notes	Sources
Compost	PLA	0.01 – 0.057	3 —●— 100 (77)	9 – 40	40 – 120	-low temp. composting results in less than 10 % biodegradation	[215,222–226]
	TPS	0.005 – 0.05	22 —●— 100 (79)	0 – 5.5	7 – 70	-low temp. composting results in low rate of biodegradation	[219–221,227–232]
	PHA	0.003 – 0.1	50 —●— 100 (81)	0 – 5	7 – 112	-higher biodegradation levels seen for PHBV than PHB	[219,223,225,233–239]
AD	PLA	0 – 0.026	0 —●— 100 (75)	0 – 10	32 – 660	-negligible biodegradation under mesophilic conditions	[240–247]
	TPS	0.003 – 0.012	21 —●— 83 (45)	0 – 35	15 – 139	-% biodegradation depends on the starch blend	[219,230,231,248]
	PHA	0.003 – 0.098	69 —●— 100 (86)	0 – 14	10 – 56	-degrades in both mesophilic and thermophilic temperatures	[219,239,253,241,243,245,247,249–252]
Landfill	PLA	0 – 0.0022	0 —●— 95 (33)	-	100 – 360	-% biodegradation is higher with increased acidity and incubation time	[216,217]
	PHA	0.02 – 0.06	10 —●— 85 (36)	0 – 3	14 – 25	-% biodegradation varies between tests due to changes in microbial activity	[217,250,254]

*biodegradation rate was determined by dividing the percent biodegradation achieved over the amount of time (in days) reported in each study. Given that each study did not collect biodegradation data the same way, it is important to note that these values do not account for differences in sample size/shape or testing methods.

4.1.2 Microbial activity

The microbial activity level and types of microorganisms to which the plastics are exposed greatly affect the rate and extent of biodegradation. The types of microorganisms present can

change drastically based on environmental conditions such as pH, moisture content, temperature, oxygen and nutrient availability, which makes repeating biodegradation tests challenging. Gutierrez-Wing *et al.* [247] noted a 50% difference between studies of PHB samples in the same environment, which they largely attributed to a difference in microbial activity levels. Given that the type of microbial organisms present depends on oxygen availability and temperature, bio-based plastics are found to degrade differently in anaerobic and aerobic environments. In general, the biodegradation behavior of bio-based plastics varies greatly due to the availability of microorganisms capable of degrading them. PHB, for example, is one of the most readily biodegradable bio-based plastics due to the large number of microorganisms that are capable of degrading PHB through both intracellular and extracellular PHA depolymerases [255]. On the other hand, few microorganisms are capable of biodegrading PLA with a high molecular weight [216]. In general, studies have found that bioplastics biodegrade more readily in composting and AD conditions as opposed to soil and marine environments, due in part to the higher concentration of microbes present and more controlled temperatures [159]. Despite the slower rate of biodegradation, biodegradable bioplastics still offer the potential to completely biodegrade in the natural environment in up to 5 years depending on the size/shape of the plastic and the environmental conditions, as opposed to non-biodegradable fossil-based plastics which can remain in the environment for centuries [256].

4.1.3. Experimental methods

The experimental methods used for analyzing biodegradation can also impact results. Factors that contribute to the greatest variation are the parameters being measured, experiment duration, and specimen surface area. The main methods for analyzing the biodegradation of a material

include (1) measuring CO₂ or CH₄ evolution, (2) determining weight loss over time, (3) measuring biological oxygen demand (BOD) (4) visual monitoring and (5) testing changes in mechanical properties. Each method is accompanied by a set of standards (Kale *et al.* [214] and Folino *et al.* [257] summarize different standards and testing methods of biodegradation). Therefore, some of the variation among results from biodegradation studies is due to the fact that weight loss measurements and visual inspections of material degradation are not directly representative of the mineralization process. The length of biodegradation studies can also vary significantly and are not always long enough to reach a maximum percent biodegradation [223,234]. Lastly, the polymer dimensions and surface area also impact the rate of biodegradation, with varying effects depending on the type of plastic. For example, Gutierrez-Wing *et al.* [247] reported an 80% decrease in the rate of degradation for PHB when thickness increased from 0.24 to 5 mm. Conversely, it has been shown that PLA is autocatalytically degradable at thicknesses above 2 mm, where an accumulation of acidic oligomers expedites the rate of degradation [215,258]. Another key difference is that PLA primarily undergoes bulk degradation at thicknesses below 7.4 cm, also known as the critical thickness ($L_{critical}$) of PLA, whereas PHB primarily undergoes surface erosion [259]. During bulk erosion, water infiltrates the bulk of the polymer and results in rapid weight loss and decrease in mechanical properties. On the other hand, surface degradation results in thinning of the polymer, where degradation is limited to the polymer/water interface [258]. For PHAs, larger surface area typically allows for faster biodegradation: Volova *et al.* [260] examined the biodegradation of PHA in marine waters and noticed that the thin films biodegraded faster than the pellets due to the larger polymer/water interface which allowed for greater attachment of microorganisms to the polymer surface.

Further, sample sizes used in the literature ranged from 100 µm thick powder to whole drinking cups thereby making it more difficult to compare biodegradation results.

4.2 Biodegradation of bio-based plastics in compost

In the studies reviewed, the range and average biodegradation for PHB and PLA were found to be 50-100% (average of 88%) and 64-100% (average of 78%), respectively, in compost conditions. Based on the composition of TPS, the degree of biodegradation among studies ranged from 22-100% [219,220]. Commercial TPS blends can vary in starch content from 20-90% which can significantly impact biodegradation behavior. For example, “class Z” Mater-Bi TPS products contain PCL, which can result in a more rapid rate of biodegradation: Bastioli *et al.* [261] observed a 90% biodegradation over 15-30 days for two different class Z Mater-Bi materials (see Appendix B, Table S5 for a more detailed list of the TPS compositions examined in each biodegradation study). The majority of composting biodegradation studies examined herein focus on industrial composting conditions which occur at 50-60°C. However, it is worth noting that PLA cannot aerobically degrade under lower temperatures such as home composting conditions because it is resistant to microbial attack until a high enough temperature is reached to begin hydrolyzation and break down the molecular weight of PLA [262]. For example, Rudnik and Briassoulis [263] did not observe any degradation of a PLA film (30µm in thickness) in home composting conditions over a time period of 11 months. However, certain pre-treatments and blends have been effective for enabling home-composting of PLA: Narancic *et al.* [264] found that PLA becomes home compostable when blended with PCL [264].

The results from the literature regarding bio-based plastics in compost are presented along with the EN 13432 standard in **Figure 6a** in order to better draw comparisons. Only 5 out of 24

studies met the EN 13432 standard [189] of 90% biodegradation within 3 months, and 4 studies were not conducted on a long enough timescale to show the maximum percent biodegradation of a material. The majority of these studies were conducted at lab-scale with controlled and monitored temperature, pH, and inoculum content, which is not representative of the variability of real-life composting conditions. Unlike many authors, Itavarra *et al.* [215] conducted biodegradation tests for PLA in aerobic aquatic conditions with controlled temperature and traditional compost without temperature control. Their results showed a 400% increase in the extent of biodegradation as well as a decrease in the lag phase from 40 days to nearly 0, for the traditional composting studies due to the rapid increase in temperature and increased microbial presence resulting in the hydrolyzation of PLA [215].

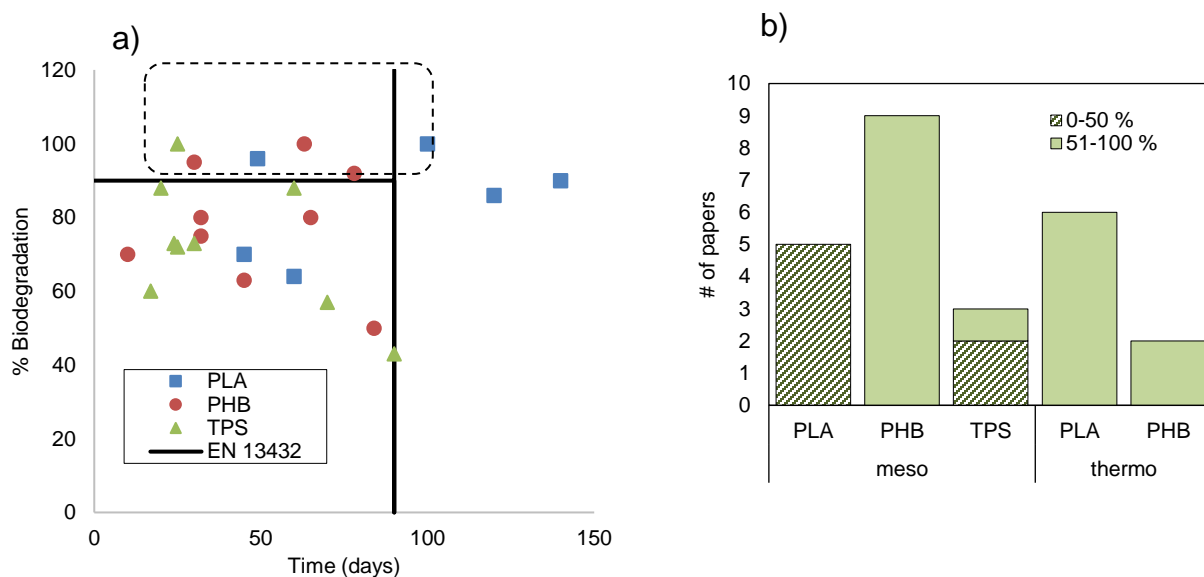


Figure 6 Biodegradability of bio-based plastics in composting and anaerobic digestion a) Summary of results from biodegradation studies of bioplastics in composting conditions. The EN 13432 standard, which states that 90% of the material must be biodegraded after 90 days, is denoted on the graph as a reference. It is important to note that the studies did not perform tests using the same methods therefore the results are not representative of differences in sample size/shape and testing method. b) Summary of results from subset of literature regarding bioplastic biodegradation in anaerobic digester conditions, where ‘meso’ indicates mesophilic and ‘thermo’ indicates thermophilic conditions. Results are summarized by achieving greater than or less than 50% biodegradation. No studies were found analyzing the thermophilic AD of TPS.

4.3 Biodegradation of bio-based plastics in AD

The literature indicates that PHB degrades readily in both mesophilic and thermophilic AD environments, while PLA only achieved significant biodegradation in thermophilic conditions. The results from the anaerobic digestion studies are presented in **Figure 6b** and broken into groups based on their compatibility with biodegradability standards. Yagi *et al.* [243,245] reported 90% biodegradation of PHB in less than 14 days under mesophilic and thermophilic conditions. Most of the PLA studies reported a biodegradation extent of less than 25% over 150 days under mesophilic conditions [245] or above 70% over 60 days under thermophilic conditions [243]. Various pre-treatment methods were also shown to increase the biodegradation for bio-based plastics. For example, Benn and Zitomer [241] found over a 100% increase in the biochemical methane potential for PLA and PHB when using elevated temperatures and alkaline pre-treatment. In addition, studies have found that co-digestion of bioplastics such as PLA with food wastes can help improve their extent and rate of biodegradation. For example, Hobbs *et al.* [210] reported a 53% weight loss for PLA in mesophilic anaerobic conditions when co-digested with food waste.

Limited studies regarding the AD of TPS were found, but the results suggested a range from 20-80% biodegradation. Once again, this large variation in biodegradation behavior is likely due to the variable compositions of TPS. Scandola *et al.* [230] observed a 20-25% biodegradation of TPS/PCL with a ratio of 0.4 in anaerobic conditions, whereas Julinova *et al.* [248] examined the biodegradation of potato starch plasticized with glycerol and found the extent of biodegradation to be approximately 70%.

4.4 Biodegradation of bio-based plastics in landfills

Despite the high rate of plastic disposal in landfills, the literature is limited in this area. Within the review conducted, only 5 papers were identified that examined the biodegradation behaviors of PLA and PHAs in landfill conditions, and none addressed the biodegradation of TPS. The limited work in this domain is likely due to difficulties with simulating the complex interactions and biological activities taking place in landfills coupled with the limited presence of bioplastics in waste streams. Shin *et al.* [217] reported that the results from repeated simulated landfill tests varied greatly for both PLA and PHB, with up to a 70% difference.

From the biodegradation studies that were reviewed, PLA was shown to biodegrade a negligible amount in landfill conditions. Kolstad *et al.* [216] concluded that there are no microbial populations present under conventional landfill conditions that are capable of degrading semi-crystalline PLA. Shin *et al.* [217] observed less than 15% biodegradation of PLA over a 100-day incubation period but found that a longer incubation time of approximately 1 year led to a mass loss of 95%, with the majority of the weight loss occurring after 6 months. This is due to the fact that PLA undergoes autocatalytic hydrolysis, meaning that the rate of hydrolysis increases with time [265]. Yet, it is possible for mass-loss experiments to over-estimate the extent of biodegradation when materials start to disintegrate and become hard to collect and measure. Therefore, more precise and thorough studies of bio-based plastics in landfill environments are necessary to better understand their potential environmental impacts.

Of the studies examining the biodegradation of PHAs in landfills, two examined the biodegradation behavior of Poly(3-hydroxybutyrate-co-3-hydroxyoctanoate) (PHBO) which is much more readily biodegradable than PHB/V. The studies examining PHBO in landfills obtained an average maximum biodegradation of 65% over an average of 22 days [250,254]. On the other hand, Shin *et al.*[217] observed less than 20% biodegradation of PHBV under 25 days and a maximum of 78% biodegradation over 180 days. In addition to landfills being difficult to model, various environmental factors have shown to have significant impacts on results. For example, Ishigaki *et al.* [266] examined the effects of aeration systems on PHBV biodegradation in landfills; their simulations suggested aeration could increase weight loss achieved by 100% over a period of 120 days.

5. Life cycle assessments

In addition to understanding the biodegradation behaviors of bio-based plastics, it is crucial to identify the assumptions used to calculate the environmental impacts from biodegradation. LCAs are a methodological process that help to understand the environmental burdens associated within each stage of the life cycle of a product or service. In this review, LCAs that analyze the cradle-to-grave life cycle of bioplastics were identified. A breakdown of the plastics analyzed within the LCAs are shown in **Figure 7**. The majority of the LCA papers reviewed evaluate PLA, PHA and TPS, but based on consumption patterns and the technical substitution potential, future research should strengthen our understanding of impacts from other bioplastics such as bio-PE and bio-PET.

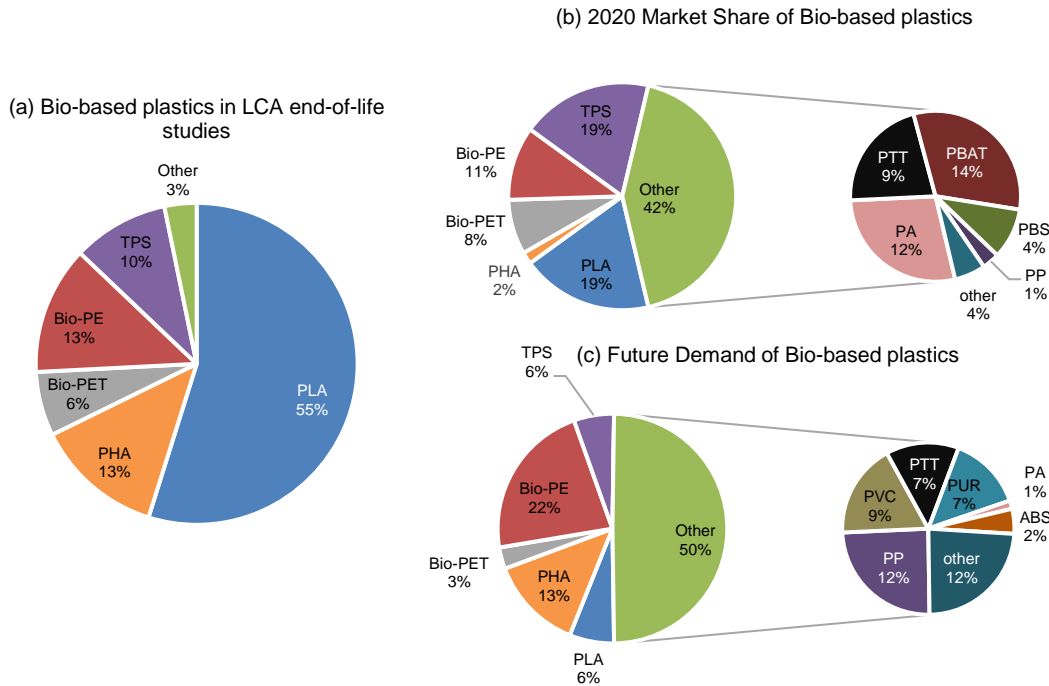


Figure 7 Pie charts showing percent breakdown of (a) bio-based plastics analyzed in LCA studies where end-of-life is addressed, (b) the 2020 market share of bio-based plastics (based on data from [161]), and (c) the future demand of bio-based plastics based on current fossil-based plastic usage (based on data from [145]) and the technical substitution potential of bioplastics (based on data from [18]).

5.1 Recycling of bio-based plastics in LCAs

Of the LCA studies that examined thermomechanical recycling, results indicated 100-130% lower GHG emissions on average when compared to all other EoL options [147,164,267,268]. However, some argue that the traditional benefits for recycling of fossil-based plastics, such as minimizing virgin material production, are not as pronounced for bioplastics. For example, Piemonte *et al.* [269] found that thermomechanical recycling of PLA resulted in 53% and 33% lower GHG emissions when compared to AD and incineration, respectively. The more modest benefit from thermomechanical recycling of bio-based plastics was claimed to be a function of reduced carbon uptake that otherwise would occur during feedstock cultivation. Further, assumptions made regarding material replacement percentages during recycling warrant further

analysis. Studies on fossil-based plastics have suggested 70% of material can be reused after recycling [270]; yet LCAs of bio-based plastics have been higher, suggesting an overestimate of replacement potential. For example, Gironi and Piemonte [271] and Piemonte [269] assumed that 90% of recycled PLA could replace virgin PLA; Rossi *et al.* [164] assumed 83% for TPS and PLA.

The influence of deterioration during the recycling process and during the use-phases of the plastics must be addressed as there are several known deterioration mechanisms that can take place during plastic exposure to temperature, moisture, or physical loading, which can alter material properties. Prolonged exposure to high temperatures and moisture can affect plastic physical aging, solvent absorption (plasticization and swelling), crystallization, stress relaxation, crosslinking, and chain scission [272]. Under increased temperature exposure, such as that during thermomechanical recycling itself, there are two prominent mechanisms to influence plastic properties. One is increased free volume, which allows for greater molecular mobility. The second is thermal degradation, resulting in effects such as chain scission, which is the main contributor to the degradation of PLA during thermo-mechanical recycling methods [273–275]. These mechanisms can result in changes such as increased brittleness [276] and altered stiffness [277]. Beyond the physical and chemical deterioration that can occur as a function of thermomechanical recycling, plastics that have already served one or more uses are susceptible to aging deterioration. For example, the chemical or physical aging of semi-crystalline polymers as a result of time elapsing at certain temperatures (e.g., secondary crystallization) can impact their mechanical properties. The issue of aging and re-processability is especially important for biodegradable materials due to their thermo-hydrolytic degradation behaviors. Baltscheit *et al.*

[278] simulated accelerated aging conditions for various transparent fully and partially bio-based plastics as well as petroleum plastics and found that materials with higher biogenic carbon content, such as PLA, aged more quickly. Future research should advance our understanding of the degradation behavior of recycling bio-based plastics.

5.2 Incineration of bio-based plastics in LCAs

The average GHG emissions from incineration from the literature were found to be approximately 1 kg CO₂-eq/kg of PLA, 1.4 kg CO₂-eq/kg of TPS and 1.6 kg CO₂-eq/kg of PHB. The CO₂ emissions can be well approximated with stoichiometry. However, the total GHG emissions of bio-based plastic incineration is still variable among LCA studies due to the multifunctionality of the byproducts: biochar, electricity, and heat. Impacts can be allocated to these products in different ways and the allocation process involves a lot of uncertainty due to differences in incineration plant electricity generation efficiencies. Due to this variability, ISO guidelines recommend avoiding allocations via system expansion [279]. Beyond the modeling of byproducts, there is discrepancy among LCA modelling of biogenic carbon. Although some studies treated incineration emissions from bio-based plastics as net-zero, it is important that LCAs present the impacts associated with biogenic carbon as the production of bio-based plastics are typically credited for carbon storage. **Table 3** provides a detailed summary of the assumptions made in each LCA study examining bio-based plastic incineration as well as the corresponding results. While GHG emissions are commonly analyzed, the human health impacts from MSWI are sometimes overlooked and highly variable among LCAs. Some researchers have found that from a life cycle perspective, incineration can lead to desirable reductions in human health impacts by offsetting the need for energy production from the grid [187]. However, this

may change in the future as there are continued shifts towards renewables. Further, given that the majority of plastics are still fossil-based, it is important to note that incineration emissions for the plastic sector as a whole could be significant compared to other waste management options.

Table 3 Summary of LCA literature on bio-based plastic incineration. The quantitative results are representative of the GHG emissions solely from EoL.

Reference	Year	Material	Assumptions	GHG (kg CO ₂ -eq/kg)
[164]	2015	PLA, TPS	-electricity replaces UCTE electricity mix, heat replaces natural gas -electric and thermal efficiencies are 14% and 41% respectively -biogenic emissions included	Without credit: PLA= 1.9, TPS = 2 With credit: PLA =0.9, TPS =1.1
[267]	2019	PLA	-incineration of PLA credited with electricity and heat displacement -calculations were done with and without counting biogenic emissions	Without credit: PLA (excl biogenic) = 0.358 PLA (incl biogenic) = 1.9 With credit: PLA (excl biogenic) =-0.4 PLA (incl biogenic) = 1.17
[280]	2011	PLA, TPS (starch/PCL), PHB	-electricity replaces European electricity grid, heat replaces natural gas -11% and 22% of total gross calorific value of waste input is exported as electricity and heat respectively (based on industry average). -biogenic emissions included	Without credits: PLA = 1.83, TPS = 1.99, PHBV = 2.12 With credits: PLA = 1.24, TPS = 1.26, PHBV = 1.31
[268]	2016	PLA	-electricity replaces electricity from the grid (US average) -electricity produced at efficiency of 17.8%. -biogenic emissions included	Without credits: PLA, PHB = 1.3 With credits: PLA = 1.2-1.3, PHB =1.2-1.4
[80]	2010	PLA	-biogenic emissions included -no credits for electricity/heat generation	PLA = 1.8
[281]	2014	PLA	-electricity replaces electricity from the grid (Thailand) -electricity generation efficiency of 30% -biogenic emissions treated as net-zero	PLA = -2.87

5.3 Composting of bio-based plastics in LCAs

Given that the emissions from compost are not generally captured and utilized as an energy source like they are in AD, incineration, and sometimes landfills, the overall GHG emissions for composting bioplastics are found to be higher than other EoL options. For PLA and PHB, composting resulted in a 7-50% and 40-85% increase in GHGs, respectively, compared to other EoL options, excluding recycling [147,155,164,268,280–282]. The LCA impacts of composting

were found to be the lowest for TPS, which, for papers that included biogenic emissions, could be due to the lower carbon content of pure starch compared to PLA and PHB. The LCAs reviewed made conservative assumptions regarding the ability of bio-based plastics to biodegrade in composting conditions relative to experimental findings: assumptions were, on average, 19%, 5% and 10% lower than the results from experimental biodegradation studies for PLA, PHB, and TPS, respectively. The biggest difference between LCA results comes from the methods for calculating emissions. For example, Rossi *et al.* [164] and Hermann *et al.* [280] included biogenic emissions in their EoL calculations leading to an average value of 1.7 kg CO₂-eq/kg (including credits), whereas Papong *et. al* [281] treated emissions from biodegradation as net zero and obtained a value of 0.06 kg CO₂-eq/kg PLA. **Table 4** provides the assumptions and corresponding results from the LCA studies examined.

Despite the variability regarding the GHG emissions of composting, other environmental impact categories show more agreement between studies. For example, due to associated nutrient runoff, composting generally results in the highest eutrophication impacts when compared to AD or landfills [210]. In addition, the cumulative energy demand of the composting process is quite high compared to landfills, requiring 100 kWh of electricity per ton of waste for composting relative to 0 kWh for landfilling. Further, composting lacks the ability of AD systems to use resulting emissions as an energy source, thus increasing relative energy inputs [210].

Table 4 Summary of LCA literature regarding bio-based plastics in industrial composting conditions. The quantitative results provided are representative of the GHG emissions solely associated with the EoL stage of the LCA.

Reference	Year	Material	Assumptions	GHG (kg CO ₂ -eq /kg)
[282]	2017	PLA, TPS	-PLA and TPS biodegrade 60%, with 95% of the resulting emissions in the form of CO ₂ , and 5% as CH ₄ -biogenic CO ₂ emissions treated as net zero	PLA, TPS = 0.3
[164]	2015	PLA, TPS	-PLA and TPS biodegrade 80% (resulting in 1.03 g and 1.09 g of CH ₄ emissions/kg plastic respectively, in addition to CO ₂) -resulting compost replaces peat -includes emissions from compost over 100 years -biogenic CO ₂ emissions included	Without credit: PLA= 1.9, TPS = 2 With credit: PLA = 1.8, TPS=1.9
[280]	2011	PLA, TPS (starch/PCL), PHBV	-compost achieves carbon and nitrogen credits for peat and fertilizer substitution - PLA and PHBV biodegrade 80%, TPS biodegrades 70% -biogenic emissions included	With credit: TPS= 1.42, PLA= 1.53, PHBV =1.77
[268]	2016	PLA, PHB	-biogenic emissions included -includes emissions from transportation and fuel for turning compost (0.44 k CO ₂ e/ kg plastic) -PLA and PHB biodegrade 90% -no credits for compost	PLA = 1.7, PHB = 1.9
[281]	2014	PLA	-PLA biodegrades 87% -biogenic CO ₂ emissions treated as net-zero -resulting compost used as soil conditioner (peat)	0.064
[155]	2020	PLA	-60% biodegradation -assuming 5% of emissions from composting are in the form of CH ₄ -biogenic emissions counted -no credits for compost	1.6
[283]	2024	PLA, PHB	-77% and 81% biodegradation of PLA and PHB, respectively. -includes electricity consumption at composting facility -biogenic CO ₂ emissions included -no credits for compost	PLA = 1.41, PHB =1.66

5.4 AD of bio-based plastics in LCAs

Due to limited use of AD systems for MSW and lack of robust knowledge regarding the impacts of bioplastics in traditional organic waste management systems, only 3 papers were identified in the LCA literature that analyzed AD as an EoL option for bio-based plastics, one of which did not contain extractable data. Based on this literature, the average GHGs for AD for all of the bio-based plastics is about the same: 1.2-1.3 kg CO₂-eq/kg [164,280]. The application of credits and the assumptions regarding the generation of excess electricity had a large effect on these results.

Table 5 summarizes the assumptions made in each LCA study and the corresponding impact on GHG emissions. On average, the applications of credits resulted in a 55% decrease in the GHGs.

For example, Hermann *et al.* [280] analyzed various EoL pathways for PLA and assumed that all of the biogas would be burned to support energy demand in the plant with excess offsetting the European electricity grid. In addition, these authors assumed that the digestate produced could be used as in soils to displace traditional conditioners and chemical fertilizers. By applying these credits, the GHG emissions for the EoL of PLA dropped nearly 55% from 1.47 kg CO₂-eq/kg to 0.67 kg CO₂-eq/kg. Similarly, Rossi *et al.* [164] assumed that the methane resulting from the thermophilic AD of PLA could be used as a substitute for natural gas to generate heat and electricity. These authors also assumed that the digestate could replace peat. Together, these credits more than halved the EoL GHGs from 2.2 kg CO₂-eq/kg to 0.9 kg CO₂-eq/kg for PLA. These large variations highlight the importance of understanding the ability of AD by-products to act as substitutes for electricity and compost.

Unrealistic modeling of the AD process in LCAs could provide misleading information regarding the environmental impacts of such processes, thus making it harder to make informed decisions regarding proper waste management techniques for bio-based plastics. All of the LCAs examined in this review assumed thermophilic conditions, resulting in estimated bio-based plastic biodegradations between 70-90%. Although the assumed extent of biodegradation in thermophilic anaerobic conditions aligns with experimental studies, the majority of existing AD systems are mesophilic due to their lower cost and ease of operation [284]. As stated previously, certain materials such as PLA are not found to biodegrade in mesophilic conditions due to the insufficient temperature. Therefore, future LCA modelling should try to reflect impacts of the current AD systems in use.

Table 5 Summary of LCA studies regarding bio-based plastics in anaerobic digestion. The quantitative results are presentative of GHG emissions strictly from the end-of-life stage of the LCA.

Reference	Year	Material	Assumptions	GHG (kg CO ₂ -eq/kg)
[164]	2015	PLA, TPS	-thermophilic conditions -biogenic emissions included -methane produced replaces natural gas for heat production -resulting biogas is 60% CH ₄ , 40% CO ₂ -digestate substitutes peat -PLA and TPS biodegrade 85.7% and 90% respectively.	Without credits: PLA, TPS = 2.1 With credits: PLA, TPS = 0.9
[280]	2011	PLA, TPS (starch/PCL), PHBV	-thermophilic conditions -biogenic emissions included -biogas burnt for electricity production, all methane captured -electricity generation efficiency of 36%, with ¼ of the electricity being used internally (28% is exported electricity). -biogas composition is 50% CO ₂ , 50% CH ₄ . -digestate substitutes peat. -PLA and PHBV biodegrade 80%, TPS 70%	Without credits: PLA = 1.47, TPS = 1.38, PHBV = 1.7 With credits: PLA = 0.67, TPS = 0.6, PHBV = 0.77

5.5 Landfilling of bio-based plastics in LCAs

Although several LCA studies incorporate landfill as an EoL option in their analysis, without biodegradation data, poorly supported assumptions were often made leading to extremely variable results. The assumptions made in each study analyzing the impacts of bioplastics in landfills are summarized in **Table 6**. The LCA studies that considered PLA in landfill conditions obtained GHG values ranging from 0.04 to 5 kg CO₂-eq/kg of PLA [155,164,268,281,282]. The highest value was reported by Papong *et al.* [281], where “worst case scenario” for GHG emissions was modeled by assuming that PLA would degrade 100% in landfill conditions without biogas capture technology. Conversely, Posen *et al.* [268] achieved the lowest GHGs (0.04 kg CO₂-eq/kg of PLA) by assuming that PLA would not degrade at all and the only emissions would come from transportation of waste. Furthermore, Benavides *et al* [155] conducted a sensitivity analysis showing that the overall life-cycle GHG emissions of PLA (from production to EoL) changed significantly depending on the degree of biodegradation assumed at EoL, with the results changing from 1.7 to 4.5 kg CO₂-eq/kg when assuming biodegradation extents of 0% and 85% respectively.

Environmental impacts of landfill disposal were also sensitive to waste composition, biogas capture technology, electricity displacement, and leachate management. For example, the GHGs calculated by Papong *et al.* [281] for PLA in landfills varied from 1.6 to 5 kg CO₂-eq/kg PLA, with values corresponding to the emissions with and without biogas capture and energy use, respectively. Due to the lack of site-specific monitoring data, the long-term emissions and impacts of landfills were modelled with limited precision. Posen *et al.* [268] and Levis *et al.* [254] modelled the environmental impacts of PHB and PHBO in landfill conditions using similar assumptions regarding extent of biodegradation (approximately 45%). However, estimates from Levis *et al.* [254] were 73% lower due to differences in assumptions regarding energy recovery. Overall, the incongruity between LCA papers highlights the need for more research regarding the degradation behaviors of bioplastics in landfill conditions as well as the need for standardization regarding the methods for modelling the environmental impacts of landfills.

Table 6 Summary of assumptions made in LCA studies regarding bio-based plastic behavior in landfill conditions and their results.

Reference	Year	Material	Landfill Assumptions	GHG (kg CO ₂ -eq /kg)
[282]	2017	PLA, TPS	-PLA: Two scenarios: (1) 0% biodegradation (2) 37% biodegradation over 100 years. Inventory based off of PET and cardboard ecoinvent landfill processes -TPS: Data from ecoinvent “packaging cardboard” landfill inventory with gas capture and flare -biogenic CH ₄ included, biogenic CO ₂ is net zero	PLA: (1) 0.05 (2) 2.81 TPS: 1.2
[164]	2015	PLA, TPS	-PLA: 1% biodegradation over 100 years. -TPS: 99% biodegradation over 100 years. -partial methane capture (49%) and use for heat and electricity (22%) -biogenic emissions included	PLA = 0.05 TPS = 6.4
[268]	2016	PLA, PHB	-PLA: 0% biodegradation, only accounted for emissions from landfill equipment and transportation -PHB: Biodegradation of PHB modelled as triangular distribution (min=41%, mode=42%, max=53%). Assuming portion (70%) of landfills have biogas capture, and a portion (50%) have energy recovery -biogenic emissions included	PLA: 0.04 PHB: 2.2 – 4.8
[281]	2014	PLA	100% biodegradation (60% of CH ₄ is captured, 40% emitted) with (1) and without (2) energy recovery. -biogenic CH ₄ is counted, biogenic CO ₂ is net zero	(1) 1.6 (2) 5
[155]	2020	PLA	Two scenarios: (1) 0% biodegradation and (2) 60% biodegradation with 75% of biogas capture/flare -biogenic CH ₄ counted, biogenic CO ₂ from captured methane net zero	(1) 0 (2) 1.8
[254]	2011	PHBO	45% biodegradation for landfill with (1) state-of-the-art gas capture technology (+ energy generation) (2) assuming 66% of landfills have gas capture and 50% of those have energy recovery	(1) -0.42 (2) 1.3

5.6 Sources of variability in EoL impacts

Due to limited and inconsistent biodegradation data for bio-based plastics at EoL, large variations were observed in the environmental impacts reported among LCA studies. The average values as well as the ranges for each bio-based plastic in each EoL stream are presented in **Figure 8**. The largest variation in results reported occurred for bio-based plastic landfilling, which is predominantly due to the lack of data for bio-based plastic biodegradation in these conditions. A substantial amount of variation for recycling was also found between studies. There are current limitations in research on loss of material performance from thermomechanical recycling of bio-based plastics, which, in turn, limits the robustness of assessments considering replacement virgin materials. For composting and AD, there is a disagreement in the literature

regarding the efficacy of by-products formed to replace traditional chemical fertilizer, which affects modeling of offsetting such products. Some studies assumed that the by-product compost or digestate could act as a soil conditioner replacement and negate the impacts of chemical fertilizer [280]. Others have argued that the compost or digestate resulting from bio-based plastic decomposition does not contain enough phosphorous, nitrogen, and potassium to act as a sufficient replacement for traditional chemical fertilizer, nor does it possess fibrous and porous textures which are necessary for nutrient retention [164]. Further, for AD, the amount of methane assumed to be captured and used as electricity, as well as the type of fuel is that is assumed to be displaced, can have a significant impact on the LCA results; however, there is currently no LCA standard for choosing an energy type to displace, leading to variable assumptions among studies [285]. Although energy types vary by region, not all LCAs utilize region-specific data, and the make-up of electricity grids can change rapidly. Therefore, standards can still be made regarding the quality of data that is used to ensure that electricity generation credits are based off of up to date, realistic electricity generation emissions for that region.

In addition to varying allocation methods and credit applications, GHG emissions are also affected by life cycle inventory data and assumptions. Life cycle inventory data for waste management systems is often sparse [286]. A recent review of organic waste management system LCAs by Morris *et al.* [285] showed that a large source of variation among composting studies resulted from differences in assumptions regarding process emissions, with alterations from management practices resulting in potent GHG emissions [285]. Therefore, it is possible that GHG results between studies varied as a result of differences in management practice assumptions.

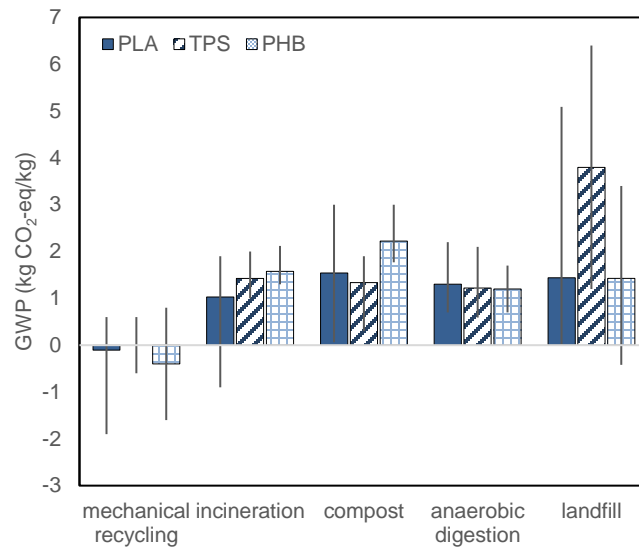


Figure 8 Summary of results from LCA studies reporting the GHG emissions of bioplastics at EoL. Bar graphs represent the mean GHG values, error bars represent the minimum and maximum values.

6. Areas for future exploration

To prevent the mismanagement of bio-based plastic waste, more informative labelling should be required for these materials based on a standardized criterion for biodegradability. Numerous biodegradation studies have found that bio-based plastics such as PLA, TPS, and PHB can degrade in industrial composting conditions; however, inadequate labeling can mislead the consumer. For example, PLA is only certified as compostable in industrial composting conditions, which takes place between 50 and 60 °C and is much higher than the temperatures for home composting, marine environments and freshwater systems. Therefore, simply labeling a product as “compostable” is likely to result in the mismanagement of waste. In Europe, the Directive on Packaging and Packaging Waste (94/62EC) states that in addition to substantiating EoL claims with references to standards, the consumer should also be informed of how to dispose of the product [287]. Further, a “reasonable portion of consumers” must have access to

the proper infrastructure for disposal, otherwise the claim is considered invalid [287]. By adopting this method of labeling, the responsibility of waste management is partially put back on the producer, rather than the consumer, which can help minimize the mismanagement of waste.

Despite potential future policy changes, a large portion of plastic waste will likely continue to be mismanaged. A recent study calculated that approximately 47% of plastic waste generated globally in 2015 ended up in the natural environment [288]. However, degradation of bio-based plastics in the natural environment requires future study to determine environmental impacts more accurately. Some bio-based plastics are found to behave similarly to traditional plastics in the natural environment; such findings have suggested a slow degradation overtime that results in the production of microplastics and nano-plastics, which can be ingested by marine life [289,290]. Although some studies have examined the biodegradation behaviors of bio-based plastics in the natural environment, there are currently no robust LCA impact categories that account for the effects of plastic debris pollution or littering in the environment [291]. In 2017, the Forum for Sustainability through Life Cycle Innovation (FSLCI) started a declaration to emphasize the need for the integration of marine ecological impacts into LCAs, specifically as a result of plastic pollution. Since then, various studies such as ones by Rajmohan *et al.* [292] and Woods *et al.* [293] have started to close the gap by forming characterization methods for environmental and human health impacts of plastic pollution. However, these studies are currently limited to fossil-based plastics and require further research before they can be more easily integrated into LCAs. Further, there is currently no standard providing pass/fail criteria for the degradation of plastics in sea water [294].

Many of the bio-based plastics that are commercially produced contain additives and plasticizers to improve their performance characteristics. For example, PLA is sometimes co-polymerized with polycaprolactone (PCL) to reduce brittleness or citrate groups to improve ductility [295]. PHB, on the other hand, is traditionally mixed with plasticizers to minimize thermal degradation and decrease the crystallinity (thereby improving toughness and softness) [295]. Although some of the mechanical properties of TPS can be improved using low-cost and non-toxic plasticizers (e.g. glycerol and water), some commercial processes use chemicals such as acetate to improve its hydrophobicity [295]. The presence and concentration of additives in bio-based plastics can impact the rate and extent of biodegradation. Further, the toxins and carcinogens inside plastic additives may get ingested through the consumption of seafood. Bishop *et al.* [62] performed a literature review of LCA papers that compared impacts of bio-based plastics to fossil-based plastics and found that 84% of the studies failed to include additives in the life cycle inventories of plastics. Furthermore, when studies included additives in the life cycle inventory, their impacts were not mentioned or modelled at EoL. Therefore, future research should analyze the impact of additives on the rate and extent of bio-based plastic biodegradation as well as on human health. Additionally, more transparent inventories of bio-based plastics and the presence and concentration of additives is critical to accurately modeling the life cycle impacts of these materials.

7. Conclusion

Bio-based plastics present a tremendous opportunity to reduce the GHG emissions of plastic production; yet the proper waste management system for these materials, which can also have significant effects on net GHG emissions, has not been thoroughly identified. In this work, the

literature on LCAs of common bio-based plastics that include EoL in the scope was examined. Additionally, studies analyzing the biodegradation behaviors of the common biodegradable bio-based plastics (PLA, PHB and TPS) in AD, compost and landfill conditions were reviewed. Concurrent assessment of these two bodies of literature was performed to identify key trends and highlight research gaps. From this combined literature review, the following conclusions were drawn:

- Bio-based plastics typically examined in LCA studies and biodegradation studies do not align well with the current and projected future consumption of bioplastics: 78% of studies analyzed PLA, PHB and/or TPS, which are expected to only make up 29% of future bio-based plastic consumption based on their current technical substitution ability and current plastic demand.
- The majority (60%) of LCA studies included landfills as an EoL option, while very few (12%) biodegradation studies examined bio-based plastics in landfills.
- The lack of understanding regarding bio-based plastic biodegradation in landfills led to many inaccurate assumptions within LCA studies; these assumptions resulted in variable and inconsistent environmental impact findings between studies.
- LCA results for bio-based plastics in AD were highly sensitive to the application of credits, which decreased the GHGs by 55% on average.
- Only 38% of biodegradation studies of bio-based plastics in compost have been conducted on timescales long enough to produce results that align with the timescale of standards for compostable packaging.

Continued growth of bio-based plastics demand is anticipated; however, if all future production of plastics was substituted with biodegradable bio-based plastics, but no changes were made to the waste management system, the overall GHGs from plastic use could increase due to the release of methane during biodegradation in landfills. To harness the potential for bio-based plastics to minimize GHGs, further research should be conducted to understand the biodegradation behavior of these materials in different environments. This need is particularly pronounced for landfills for which there are limited published results, but these are expected to be a key pathway for material disposal based on current waste management practices. Furthermore, policymakers should focus on making proper disposal pathways for bio-based plastics apparent and accessible to consumers to reduce the mismanagement of plastic waste

Chapter 4. Global scale carbon dioxide removal (CDR) with bio-based plastics

Authors note: This chapter comes from the publication “Using biogenic resources to make plastics a global carbon sink: a roadmap for sustainable decarbonization by 2050” recently submitted to *PNAS*

Abstract

There is a rising urgency to decarbonize plastic production given its high carbon footprint and rapid growth in demand. Here, we highlight the numerous pathways that could support plastics acting as a carbon dioxide removal (CDR) strategy on a global scale by 2050. Due to their high technology-readiness and to promote a circular bioeconomy, we focus on the utilization of bio-based plastics and consider potential market replacement, energy resources for production, as well as waste management practices to systematically assess how plastics can act as a carbon-uptake mechanism. Our findings suggest there are over 100,000 combinations of strategies that could be employed to achieve CDR in plastics with the greatest uptake from the scenarios considered leading to ~260 Mt of annual CDR by 2050. To achieve CDR with plastics, pathways must include (1) a minimum of 60% bio-based plastics (2) a minimum of 70% renewable energy, or (3) a minimum of 50% recycled plastics. Considering resource availability and technological characteristics, we generate a roadmap to evaluate full-scale implementation of bio-based plastics and highlight CDR pathways. We find that a 58% reduction in annual GHG emissions from the plastic sector is possible to achieve in the near term (2030), and by 2040, the plastic industry could become a carbon sink with 80% bio-based plastics and a 46% recycling rate.

1. Introduction

The high carbon footprint of plastics, driven by their reliance on fossil-fuels as both a feedstock and energy-source, resulted in roughly 2 Gt of carbon dioxide equivalent (CO₂e) emissions in 2019 [296]. In part driving these high cumulative emissions, the rate of increase in plastic production has outpaced all other bulk materials and is expected to double in annual production quantities by 2050 [41]. Due to an increasingly largescale of expected production, plastics are on track to contribute to 15% of the global carbon budget by 2050 [9]. To achieve the 1.5°C and 2°C targets set by the Intergovernmental Panel on Climate Change (IPCC), a drastic shift in the way we currently produce and dispose of plastics is urgently needed. It has been theorized that plastics can act as a carbon sink when combining renewable energy, 100% recycling, and fully bio-based or CO₂-based feedstocks for plastic production [41,42]. However, the ability to successfully implement the use of renewable energy, alternative feedstocks, and recycling technologies will depend on various factors such as resource availability, energy demand, and the market potential of different plastic technologies. Here, we study the cumulative effects of factors such as electricity source, feedstock source, waste management practice, market potential of various plastics, and biogenic resources necessary on the ability of plastics to act as a CDR mechanism at a global scale. Notably, we examine bio-based plastics, as opposed to carbon-utilization plastics acting as reservoirs of captured carbon, to potentially create atmospheric CDR systems (referred to herein as a “CDR plastics”).

In this work, we utilize harmonized life cycle assessment (LCA) models [297] to quantify CDR pathways. Namely, we consider three biodegradable plastics, polylactic acid (PLA), thermoplastic starch (TPS), and polyhydroxybutyrate (PHB), as well as 6 non-biodegradable bio-

based plastics: polyethylene terephthalate (Bio-PET), high density polyethylene (Bio-HDPE), polyvinyl chloride (Bio-PVC), polypropylene (Bio-PP), polyurethane (Bio-PUR), and polytrimethylene terephthalate (Bio-PTT). The GHG emissions associated with end-of-life (EoL) management of bio-based plastics is also considered for various treatments including: landfill, incineration, composting, anaerobic digestion, thermomechanical recycling, and chemical recycling [37]. To model the impact of implementing various technologies and waste management scenarios, we assess the potential utilization of each plastic type at a global scale. By examining these factors and the percent of energy supplied by renewables, various CDR scenarios are identified as are thresholds beyond which carbon uptake would occur. We further utilize technology readiness levels (TRLs) and a resource availability assessment to determine the level of GHG reductions that could be achieved in the short (by 2030), medium (by 2040), and long term (by 2050) (see details in the Methods).

2. Methods

2.1. Life cycle inventories

Cradle-to-gate life cycle inventories for nine different bio-based plastics, including three biodegradable plastics (PLA, PHB , TPS), and 6 non-biodegradable bio-based plastics (Bio-PET, bio-HDPE, Bio-PVC, bio-PP, bio-PUR, and bio-PTT), are utilized from our prior efforts in deriving harmonized plastics datasets [297]. The GHG emissions from these inventories, as well as permutations with varying energy grids, are used to represent the projected environmental impacts for bioplastics from 1st, 2nd and 3rd generation feedstocks. In this work, 2nd and 3rd generation feedstocks refer to non-edible feedstocks that do not compete with food production and feedstocks with a negligible land footprint, respectively. The cradle-to-gate life cycle

inventories of fossil-based plastics are derived from previously established datasets [73], and we have adapted these inventories to ensure corresponding allocation methods, cut-off rules, energy grids, and other modeling assumptions are the same as the bio-based plastics inventories.

End-of-life impacts for biodegradable bio-based plastics are determined based on a literature review of experimental biodegradation studies of bio-based plastics [37]. This review includes maximum biodegradation rates for each of the plastics considered in this work under varying disposal conditions (landfill, anaerobic biodegradation, composting). Given that the biodegradation rate of biodegradable plastics varies greatly depending on environmental factors (such as temperature, moisture content, and oxygen availability), as well as material characteristics (such as material thickness and surface area), these values are analyzed using a Monte Carlo simulation ($n = 1000$) to capture the range of potential emissions that can occur. Namely, the maximum level of biodegradation observed within a year for each plastic under different conditions was varied using normal distributions. Due to the lack of data surrounding the behavior of TPS in landfill conditions, biodegradation data from anaerobic digestion studies are used. The median values resulting from these distributions are then used as inputs to the model to determine the lifecycle impacts of biodegradable materials. An attributional approach is utilized to determine the environmental impacts for end-of-life treatment, in line with cradle-to-gate impact assessment methodology used herein. No ‘credits’ (i.e., negative CO₂ emissions) are applied for the generation of energy from incineration or anaerobic digestion (AD), given that the share of renewable energy is expected to continue to increase in the future. Similarly, given the uncertainty of the impact of bio-based plastics on resulting compost quality, no credits are applied for the generation of fertilizer for the anaerobic digestion or composting scenarios.

Certain modeling assumptions were imposed for end-of-life management pathways to ensure reliable results. On average, roughly 70% of global landfilled waste is currently sent to an uncontrolled landfill or disposal environment without biogas capture [194]. The remaining 30% go to a landfill with biogas capture and flaring. This approximate statistic aligns with more detailed monitoring at national levels. For example, according to the USEPA, only 500 out of the 2,500 landfills that are monitored nationally currently have landfill gas capture technology [298]. Therefore, in this model, it is assumed that roughly 80% of landfilled plastics are sent to a landfill without biogas capture. The make-up of thermophilic (high temperature) and mesophilic (low temperature) anaerobic digestion systems were assumed to be the same as the European average, 43% and 57% respectively [299]. These values were chosen due to the availability of data and the prevalence of anaerobic digestion in this region. In general, it is conservative to assume a lower proportion of thermophilic relative to mesophilic anaerobic digesters globally given their higher operating costs [300]. The life cycle inventory for thermomechanical recycling of all plastic (both bio-based and fossil-based) is assumed to be the same and is extracted from existing datasets [73] to remain consistent with other life cycle inventories modeled. The life cycle inventory for chemical recycling was obtained from Jeswani *et al.*, which provides data for the pyrolysis process for mixed plastic waste and supported a consistent modeling effort [301]. This pyrolysis inventory includes energy requirements for pyrolysis but does not include treatment and refining of oil to produce new polymers. A cut-off approach is utilized for both recycling inventories, wherein only the impacts of plastic waste treatment is included (no downstream processing of recyclates, or credits for replacement of virgin plastic is considered).

2.2. Identifying carbon dioxide removal pathways

2.2.1 Variables considered

The variables considered include: (a) the fraction of plastic coming from bio-based resources; (b) the fraction of energy coming from renewable resources (modeled herein as electricity being satisfied by wind, and heat being satisfied by a bioenergy); (c) the distribution of waste management options for biodegradable plastics; and (d) the distribution of waste management options for non-biodegradable plastics. Waste management options for biodegradable plastics include: (a) composting; (b) incineration; (c) anaerobic digestion; (d) landfilling; (e) thermomechanical recycling; and (f) chemical recycling. For non-biodegradable plastics, the waste management options at end-of-life include: (a) incineration; (b) landfill; (c) thermomechanical recycling; and (d) chemical recycling.

2.2.2. Production and end-of-life impacts of bio-based plastics

Cradle-to-gate impacts for bio-based plastics are derived from a comprehensive bottom-up LCA study that includes detailed inventories and results for bio-based plastics capable of replacing 80% of the current plastic market [297]. This study examined 1st, 2nd, and 3rd generation feedstocks for bio-based plastic production. When examining the total possible CDR pathways, an average value for the cradle-to-gate impacts for 2nd and 3rd generation feedstocks for each bio-based plastic was used. For PHB from landfill biogas, carbon credits were applied assuming that 50% is in the form of avoided methane emissions (e.g., a global warming potential credit of 28 kg CO₂e/kg), and 50% is in the form of avoided CO₂ emissions. Although the majority (80%) of landfills do not have gas capture technology in place, we make a conservative estimate for possible avoided methane given that other sources of biogas that could be utilized for PHB

generation, such as wastewater treatment facilities, anaerobic digesters, or natural gas plants, all of which may have gas capture in place. First generation feedstocks were not considered when determining CDR pathways given the need to limit competition with food in the long-term. However, when investigating near-term solutions for the roadmap, impacts from 1st generation bio-based plastics are considered based on their technology readiness. See Appendix C, Supplementary Data 3 for a full list of production impacts of bio-based plastics with and without renewable energy. Given that this dataset only covers 80% of the bio-based plastic market, the remainder (namely cellulose films, Bio-polyamide (PA), Bio-acrylonitrile butadiene styrene (ABS), Bio-polybutylene (PB), Bio-polyacrylates, and Bio-epoxy resins) are assumed to have impacts equal to the average of the other bio-based plastics.

2.2.3 Assumptions/limitations

Only scenarios leading to overall GHG emissions below $-0.1 \text{ CO}_2\text{e/kg}$ were considered. This value was chosen to limit results to scenarios that contribute to relatively significant carbon uptake, and to conservatively capture effects of uncertainty. A maximum recycling rate of 90% is assumed. This assumption was based on an expectation that there will always inherently be some losses to the environment/landfills. We note this assumption is a slightly more conservative estimate than what has been assumed in previous studies examining the carbon uptake potential of plastics, which have noted higher recycling rates [42].

Based on the mechanical performance characteristics of bio-based plastics, they are currently capable of replacing 90% of the fossil-based plastic market [18]. See Appendix C, Supplementary Data 2 for a detailed breakdown of the substitution capability of various bio-

based plastics. A limitation of 90% market replacement is partially due to the fact that fully bio-based alternatives have not yet been identified or have remained in the lab-scale for some plastics, including polystyrene (PS), polycarbonate (PC), and polymethyl methacrylate (PMMA), as well as some important chemical building blocks such as toluene di-isocyanate (TDI) and methylene diphenyl di-isocyanate (MDI), which are important inputs for bio-based PUR. Partial bio-based alternatives have emerged in the market for some of these materials (Mitsubishi started producing partially bio-based PC from biomass [302]) therefore it is possible that, upon further research and development efforts, more of the plastic market could be bio-based, but a conservative estimate is made herein assuming a maximum of 90% bio-based plastics.

Renewable energy scenarios are modeled using inventories for wind and biogas to cover all electricity and heat requirements (as modeled in [303]). Alternatively, the non-renewable energy scenario uses an electricity grid modelled after the 2018 global average (see Appendix C, Supplementary Data 10). Only processes that contributed to at least 5% of overall GHG emissions when using the original inventories are assumed to be met by renewables. Processes that contributed less than 5% of total GHG emissions were modeled with the original energy resources. For example, if the construction of the chemical plant has a marginal impact of less than 1% of the overall GHG emissions of a bio-based plastic production process, the energy-grid is not changed within the life cycle inventory for the chemical plant construction.

The model for “landfill” as waste management option is considered to also capture any plastic losses to the environment. Further, it is assumed that the rate at which plastics were sent to landfills for both biodegradable and non-biodegradable plastics would not be lower than 10%.

This 10% is implemented to reflect inherent losses that are assumed to occur either via losses along the waste management supply chain process, or directly from microplastic sources that are hard to control such as tire wear and personal care products [304]. Furthermore, a landfilling rate greater than 10% is not investigated in order to focus only on CDR pathways that promote a more circular economy and reduce the strain on biomass resources.

It was assumed that the maximum thermomechanical recycling rate for both biodegradable and non-biodegradable plastics was 60%. A 60% cap on thermomechanical recycling was meant to capture the fact that only thermoplastics are suitable for thermomechanical recycling, which make up roughly 85% of the 2023 plastic market [305], and that there is an assumed sorting efficiency of 75% [42,306] given the prevalence of contaminants and mixed plastic waste streams. As such, to reach 90% recycling rates, the remainder of recycling is achieved via chemical recycling. Although chemical recycling is currently energy-intensive and expensive, scenarios are examined wherein up to 90% of plastic is fully treated via chemical recycling.

2.3. Roadmap for CDR plastic

It is assumed that the demand for plastics is going to continue to increase at a rate of 4%/year from now to 2050. We also assume that the quantity of plastics reaching end-of-life each year is equal to the quantity of plastics being produced. Although there are plastics that are used in long-term applications such as construction and transportation, we made this assumption to have a “worst-case scenario” estimate for end-of-life emissions. It is important to note that accounting for the longer use-phase of plastics, especially when bio-based, could lead to lower overall GHG

emissions. It is also assumed that energy requirements for plastic production can be satisfied by renewables in the near term (2030), based on technology readiness.

2.3.1 Bio-based plastic market assumptions

The implementation of bio-based plastics within the roadmap was determined based on technology readiness levels as well as resource availability. Bio-based plastics that are currently at a TRL 9 and being produced at full scale include PLA, Bio-PE, TPS and Bio-PVC. For example, NatureWorks, the largest producer of PLA, has a capacity of 150,000 metric tons (t) and is in the process of constructing an additional manufacturing plant in Thailand, which would expand capacity by an additional 75,000 t [307]. Other major PLA producing companies include TotalEnergies Corbion (capacity of 75,000 t) [308] and Futerro (current capacity of 100,000 t) [309]. Major producers of TPS blends include Novamont (capacity of 110,000 t) [310], Kuraray [311], and Biotec (capacity of 30,000 t) [312], with products containing a bio-based content of 40-69%. It is important to note that all these companies currently utilize 1st generation crops, such as corn and sugarcane, in their production processes. However, we find that even if all PLA and TPS were produced with corn, it would amount to a demand of less than 4% of global annual corn production (See Appendix C, Supplementary Data 5 for full resource availability results). Finally, various petrochemical companies have expanded their production line to include bio-based polyethylene such as Braskem [313] and Borealis [314], and Bio-based PVC, such as Ineos [315]. Although these materials were traditionally produced using sugarcane, Borealis and Ineos utilize waste vegetable oil or corn stover as feedstocks for production.

Bio-based plastics that are only produced on a prototype/field scale or have limited feedstock availability are assumed to be at TRL range of 5-7. In the roadmap, we consider these plastics to be implementable by the midterm (2040). Fully bio-based PET materials are currently being produced on a prototype scale (such as Coca-Cola plant bottle [316]). Although PHB is currently being produced on a commercial scale [317], most companies rely on sugar from sugarcane as a feedstock (a 1st generation feedstock). To reach full-scale production for PHB that would satisfy 11% of the global plastic market, this feedstock pathway would require using 42% of globally available sugar production, which would result in significant competition with food production. However, companies producing PHB from waste (such as Mango Materials [318] which makes PHB from waste biomethane), are in the process of scaling up production. Bio-based polyol, a key component for Bio-PUR, is currently being produced on a commercial scale but is typically made from vegetable oil, or corn, which would have to compete with food resources to meet PUR demand [319]. Similarly, Bio-PP is currently being made on a commercial scale from waste vegetable oil [320], but the availability of resources is roughly 200 times lower than necessary to meet PP demand. However, it is expected that with proper research and development efforts, barriers such as these will be better understood and potentially overcome by 2040.

Bio-based plastics that are still being developed on the lab scale are assigned a TRL in the range of 1-4, and they are assumed to be implementable by 2050. This set of plastics includes Bio-PTT, Bio-PUR, PLA, TPS and Bio-PET from 2nd generation feedstocks. Furthermore, bio-based plastics that lack sufficient publicly available life cycle inventory data, such as fully bio-based PA, and bio-based ABS, are also assumed to be implementable in 2050. See Appendix C, Supplementary Data 5 and 6 for resource availability results and TRL's of the bio-based plastics.

2.3.2 End-of-life assumptions

Given that biodegradable bio-based plastics currently only make up a fraction of the 1% of the plastic market that is composed of bio-based plastics, composting and anaerobic digestion facilities do not have systems in place to differentiate these materials from their non-biodegradable counterparts. Furthermore, given the small volume of biodegradable, bio-based plastics, consumers are not aware of how to dispose of them due to lack of exposure. Therefore, it is assumed that composting and anaerobic digestion will only become suitable by 2040 when biodegradable plastics make up 22% of the global plastic market (based on the above stipulated assumptions in this roadmap), amounting to roughly 170 Mt of biodegradable plastics entering the waste stream.

Chemical recycling is currently being used by some companies for treatment of individual plastics such as PLA [321]. Additionally, some companies such as BASF are investing in the development of chemical recycling processes that handle mixed plastic waste [322]. However, given the high-cost and small-scale use of current chemical recycling systems, it is assumed to be implemented only in the long term (2050) to help minimize landfill rates.

3. Results

3.1 Pathways to carbon dioxide removal

Our findings show there are over 100,000 different scenarios that could lead to CDR plastics based on the assumptions and variables examined herein. Scenarios were determined by running an algorithm for the 11 million total combinations, using 10% increments for each variable (see

Methods for detailed assumptions). A maximum reduction of roughly -1.3 kg CO₂e/kg plastic can be achieved using 100% renewable energy, 90% bio-based plastics, and 90% recycling. However, there is notable flexibility among the required share of bio-based plastics, the fraction of renewable vs. non-renewable energy, and the type of waste management treatment that can be applied while still reaching global CDR. Thresholds beyond which CDR would occur are highlighted in **Figure 9**; a full list of these scenarios can be found in Appendix C, Supplementary Data 8. This degree of flexibility is noteworthy given the potential difficulty in achieving net-zero energy emissions, 90% recycling rate, and a fully bio-based plastic market simultaneously in a timely manner. Given the vast number of scenarios leading to CDR, herein we focus on scenarios that allow for the minimum thresholds required for renewable energy (Figure 9b) and bio-based plastic content (Figure 9c), and the maximum threshold for incineration (Figure 9d). It is important to note that each of these scenarios are mutually exclusive and therefore cannot lead to CDR if implemented simultaneously.

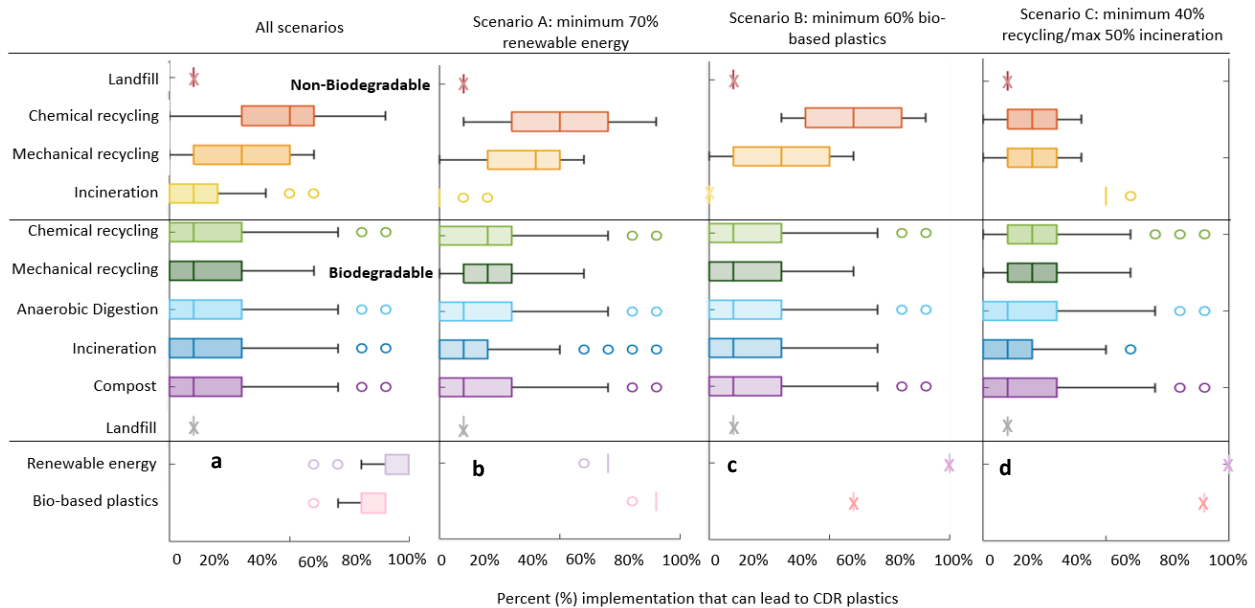


Figure 9 Summary of notable scenarios that lead to CDR for plastics globally. Box plots represent the probability (out of the total number of CDR scenarios) that a given level of implementation of the

strategies on the y-axis, will lead to CDR for the plastic industry as a whole. Stars indicate single values (e.g. for scenario B, the bio-based plastic market share is held constant at 60%). Note that these scenarios are mutually exclusive and cannot be true at the same time. Panel (a) presents boxplots summarizing mutually exclusive values for each variable that are capable of leading to CDR. Panel (b) highlights scenarios capable of leading to CDR when the minimum value of 70% renewable energy is used. Panel (c) highlights scenarios that are capable of leading to CDR when the minimum value of 60% bio-based plastics is used. Panel (d) highlights scenarios that are capable of leading to CDR when the minimum value of 40% recycling (mechanical + chemical) is used. ‘Renewable Energy’ refers to the percent of the energy demand being sourced from renewable energy vs the 2018 global average electricity grid. ‘Bio-based plastics’ refers to the percent of the plastic market that is produced using bio-based resources instead of fossil feedstock.

3.1.1 Bio-based market share

We find that a minimum of 60% of the plastic market needs to be bio-based to achieve global CDR. This condition necessitates 100% renewable energy and an 80% recycling rate of plastics; however, with more than 60% bio-based plastics on the market, there is more flexibility in the other factors. This outcome is notable given that, despite bio-based plastics being around since the 1850s [323], the growth in bio-based plastics has been slow, amounting to only 1% of the petroleum plastic market. This slow adoption suggests a growth in the bio-based plastic market will likely require pronounced policy mechanisms to drive adoption, such as incentives.

Furthermore, there might be several limitations to full adoption of bio-based plastics. For example, some commodity plastics, such as polymethyl methacrylate (PMMA) and PVC, do not have commercialized, fully bio-based alternatives available yet [324,325]. While not limited by technology readiness, some bio-based plastics, such as PHB, are expensive to produce and utilize 1st generation feedstocks, or feedstocks that compete with food production [326]. Not requiring a full transition to bio-based resources is also notable from a resource availability perspective.

Although we find that the current supply of biomass residues is sufficient to meet the demand for some bio-based plastics (see Appendix C, Supplementary Data 5), a cumulative global shift towards a more bio-based economy is expected to put a strain on resources [327], making it

difficult to keep up with plastic demand. Finally, although novel technologies such as CO₂ capture and utilization could be utilized as a method for bio-based plastic production, these technologies are not currently viable given their high cost and energy requirements [328].

3.1.2. Flexibility of energy grid

A minimum of 70% of the energy supply for plastic production needs to come from renewable sources, assuming the rest is satisfied using the 2018 global average electricity grid, to reach global CDR. This condition necessitates: (1) a minimum recycling rate of 70% is achieved; and (2) a minimum of 80% of the plastic market is bio-based. This minimum threshold of 70% renewable energy is pertinent given the notable energy demand for the petrochemical industry (amounting to ~30% of global final industrial energy use, with plastics being its main product) [29]. Compounding this issue, a shift to bio-based plastics may also require high energy demands as a function of agricultural practice needed for the biogenic resources. For example, the Haber-Bosch process for ammonia production, which is required for many agricultural processes, currently utilizes 2% of total energy consumption worldwide [329]. This notable energy demand is partly due to the high temperatures above 700°C and high pressures above 200 bar that are required for such processes [115]. Although some solar thermal technologies can reach temperatures requirements up to 2000°C [330], solar thermal energy currently only makes up a fraction of the 2.5% of the global energy supplied by renewables [136]. Therefore, plastic production may continue to rely on the use of fossil fuels until the global capacity of renewable energy generation can meet the energy demands of the plastic sector and support cultivation of requisite biogenic feedstock resources.

3.1.3. Flexibility of waste management

Various waste management strategies result in plastics acting as a global CDR mechanism. For example, up to 50% of non-biodegradable plastics can be incinerated assuming the remainder is recycled, and both 100% renewable energy and a 90% bio-based plastics market is achieved. This ability to have notable CO₂ emissions through combustion processes and still contribute to CDR plastics can support a carbon-uptake transition without causing significant shifts in other practices. This is pertinent given that incineration is a common waste management solution. In Europe, more than 40% of plastic waste is currently incinerated due to increasing policy efforts to reduce landfilling of plastics [331]. Incineration is also a common fate for plastic residues at material recycling facilities due to the relatively low sorting efficiency, of around 50%, even when economically viable sorting processes are optimized [332]. Further, roughly 2 billion people worldwide lack access to waste collection facilities and, therefore, utilize open burning of plastic waste as a disposal method [333]

It is important to note that even if all other strategies are incorporated, such as 100% renewable energy and fully bio-based plastic markets, we will still need to achieve a minimum of 40% recycling to reach CDR plastics while limiting landfill disposal to 10%. While thermomechanical recycling can be used as a method to effectively recycle thermoplastics, which make up ~85% of the plastic market [19], the global average recycling rate is currently less than 10% [334]. This disparity highlights the need for drastic and immediate changes to waste management systems globally to allow CDR to be achieved for plastics. Currently, the expense of thermomechanical recycling is unfavorable given the low cost of virgin materials, high cost of manual sorting, and the low-value or degraded performance characteristics of mechanically recycled plastics [335].

Therefore policy efforts such as extended producer responsibility laws [336,337], recycled-content targets [338], or packaging taxes [339], may be necessary to re-shape the global plastic waste management system [340].

Although chemical recycling would help to address some of the issues associated with contaminated and mixed plastic waste streams, it is currently a very energy- and cost-intensive process, and the technical and economic feasibility of large-scale implementation still needs to be assessed [341]. In this work, we consider the impacts of chemical recycling based on a pyrolysis process for mixed plastic waste. However, we note pyrolysis might not be a viable end-of-life management option for some materials (such as PET or PVC), due to the generation of harmful thermal degradation products [342], and modeling efforts to reflect other chemical recycling routes should be developed in future work.

For biodegradable plastics, anywhere from 0-90% of the material (assuming 10% is always landfilled or lost to the environment) can be treated with any end-of-life scenario (AD, compost, incineration, recycling, or landfill) and still allow for CDR globally. Yet given the different quantities of GHG emissions resulting from each of these end-of-life pathways, the degree to which the other factors (such as renewable energy) must be implemented varies depending on the end-of-life scenario for biodegradable plastics. For example, since incineration emissions are notably high for plastics, if 90% of biodegradable plastics are incinerated, then 70% renewable energy and 60% bio-based plastics would need to be implemented to reach CDR. The flexibility among biodegradable plastic waste management options is notable given the technological difficulty associated with bio-based plastic waste treatment as a result of (1) the lack of

consumer awareness on proper disposal methods for biodegradable plastics [343,344] and (2) the lack of adequate separation technology at organic recycling facilities needed to differentiate between biodegradable and non-biodegradable plastic [345]. For improved end-of-life management of biodegradable plastics, identification and separation steps need to be incorporated into commercial composting and AD facilities, and consistent, standardized labeling of bio-based plastics needs to be implemented to improve separation at the source.

3.2 Roadmap for creating carbon uptake in the plastics industry

Given the vast number of CDR scenarios for plastics, we present a roadmap based on TRLs and resource availability to 2050 (

Figure 10). TRLs are based on the United States Department of Agriculture definitions [346], and resource availability data are from the Food and Agricultural Organization 2020 statistics [72]. While these strategies do not need to be implemented at this scale or in this order, this analysis suggests that pathways to net-uptake in the plastics industry are feasible within the coming decades.

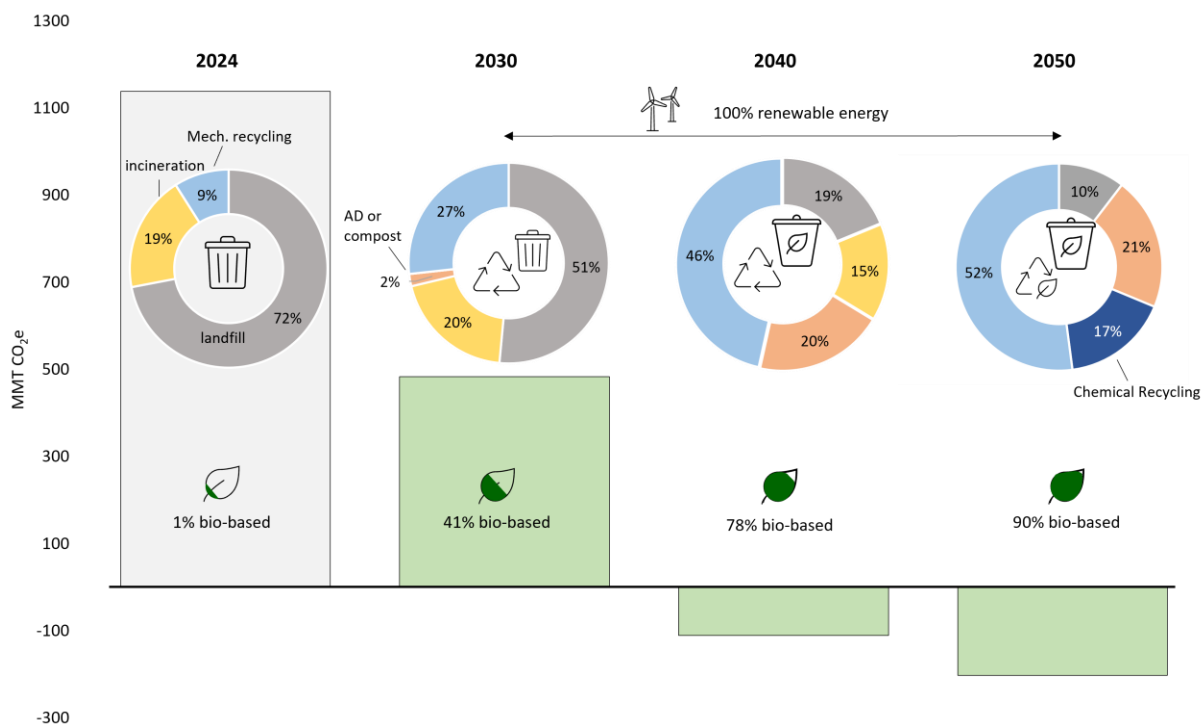


Figure 10 Roadmap for achieving CDR plastics by 2050, considering both production and end-of-life mitigation strategies. Technologies are implemented based on their technology readiness level and resource availability. Source data is available in Appendix C, Supplementary Data 9.

In the near term (e.g. by 2030), a 57% reduction in global GHG emissions associated with plastic production could be achieved via: 41% substitution of fossil-based plastic with bio-based plastics, 100% renewable energy, and 27% thermomechanical recycling. A 41% bio-based plastic market can be achieved by using PLA, TPS, Bio-PVC and Bio-PE, all of which have full-scale commercial production capabilities (see Appendix C, Supplementary Data 6). Further, this level of substitution is feasible from a resource availability perspective, requiring only 55% of available corn stover (e.g. corn stover not used as a soil amendment), and roughly 8% of reclaimed potato starch produced globally (see Appendix C, Supplementary Data 5). While the technologies and resources are available for this replacement rate, European Bioplastics [347] predicts that global bio-based plastic production will only reach 6.3 Mt by 2027, roughly 25 times less than the ~165 Mt of bio-based plastic production required to reach this 2030 target.

However, these projections are based on current market behavior. When looking strictly at technological availability, the European Technology platform for sustainable chemistry estimates that as much as 30% of the chemical industry in Europe could be sourced by renewables by 2025 [348]. These findings suggest the need for strong policy incentives and/or regulatory actions. A thermomechanical recycling rate of 27% could be achieved assuming policy mechanisms are introduced to incentivize recycling and improve sorting efficiency of plastic waste. This recycling rate aligns with goals on both regional and global scales; (1) in Europe, the plastic industry aims to increase recycling to 25-58% by 2030 [349,350], (2) the United States Environmental Protection Agency (USEPA) is targeting a 50% recycling rate of all materials by 2030 [351], and (3) the United Nations (UN) recently reported targets for a 20% recycling rate for short-lived plastics by 2030 [15].

Globally, a carbon-negative plastics industry can be achieved in the mid-term (e.g. 2040) by increasing the bio-based plastic market share to nearly 80% and by limiting landfilling of all plastics to 20% (either via recycling or composting and anaerobic digestion). Although composting and anaerobic digestion are commercially available technologies, they are currently not suitable for plastic waste, and therefore, this modeling effort reflects these technologies as being implementable in 2040. This combination would result in -110 MMT of CO_{2e} emissions/yr from the plastic industry in 2040. Bio-based plastics that are considered suitable for this midterm goal include Bio-PET, Bio-PTT, Bio-PP, PHB and Bio-PUR, (in addition to the bio-based plastics introduced in 2030) given their proximity to full-scale commercialization. This level of substitution is doable from a resource availability perspective, requiring roughly 86% of available corn stover, 8% of reclaimed potato starch, 64% of used cooking oil, and roughly 40%

of global biomethane production. The one exception is Bio-PP production from used cooking oil, which would require over 200 times the current supply. However, given that companies such as Borealis are in the process of expanding production to meet higher demand [320], it is assumed that alternative and /or more efficient production routes will be available by 2040. A recycling rate of 46% by 2040 is in-line with estimates in the literature, such as the Ellen MacArthur foundation, which calls for a 67% recycling rate by 2040, Plastics Europe, which targets a 46% recycling rate by 2040, and the UN, which estimates a 56% recycling rate by 2040. Further, reaching an 80% bio-based plastic market by 2040 aligns with the United States' goals to commercialize bio-based materials to substitute 90% of today's plastics within 20 years [14].

Although CDR is achieved in the midterm goal, this scenario still relies on roughly 15% of plastics being incinerated, 20% being landfilled, and roughly 20% of plastics made from fossil-fuels. In the long-term (2050) scenario, to create a more circular economy, recycling (using renewable energy), alongside a maximum substitution of bio-based plastics (90%), can be employed to further reduce emissions. Given the technical readiness of thermomechanical recycling, this value is assumed to be maximized to treat up to 52% of plastic waste by 2050. This value reflects the estimated market share of non-biodegradable thermoplastics (~70%) in 2050 combined with a 75% assumed sorting efficiency. This long-term combination of mechanisms may help minimize adverse environmental impacts associated with landfilled plastics [352], while simultaneously resulting in an annual carbon storage of ~260 Mt. In addition, it helps to conserve resources and increase the availability of bio-based resources for other applications, which will be increasingly important as the global population grows to 10 billion in 2050, associated with significant increases in crop demand [353].

Following the targets for renewable energy, bio-based content, and waste managements highlighted in this roadmap, over 3 Gt of CO₂e could be avoided in 2050 alone compared to a business-as-usual scenario (Figure 11). Further, this pathway could shift the plastics industry from being 15% of the carbon budget to a CO₂ removal strategy. Previous literature has reported the potential for low-carbon or CDR plastics. However, this study fills important research gaps left outside the scope of previous work by (1) incorporating the impacts of CH₄ and N₂O emissions associated with bio-based plastic production, (2) examining the utilization of non-edible bio-based feedstocks for plastic production rather than CO₂ feedstocks or food products, and (3) incorporating technology readiness levels and resource availability to provide a timeline of feasible mitigation strategies.

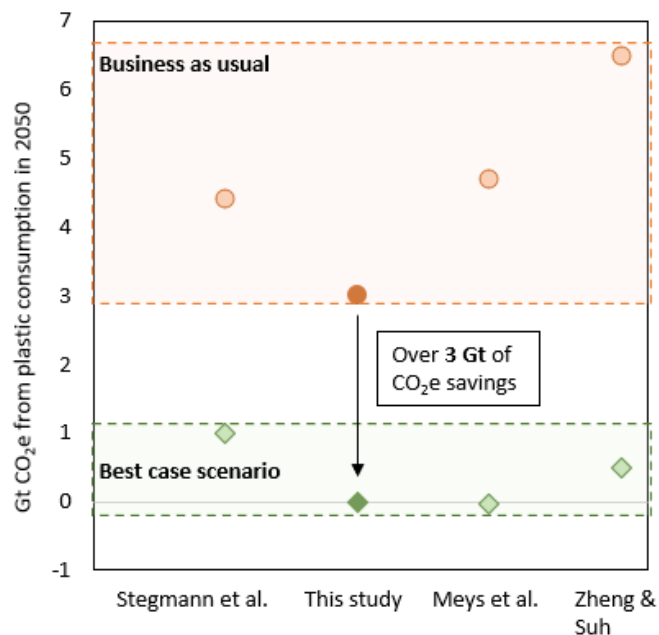


Figure 11 Comparison of roadmap results from this study to future fossil-based plastic life cycle emissions in a business-as-usual scenario. For this study, “Best case scenario” refers to a scenario in which 90% of the plastic market is bio-based, 90% of plastic is recycled, 10% is landfilled or lost to the environment, and 100% renewable energy is utilized. The shaded regions show the range of expected emissions under a business-as-usual approach (orange), and a best-case-scenario approach (green).

Here, business-as-usual is modelled assuming production and end-of-life emissions for plastics remains the same as present day, and the only change is the increase in plastic consumption. However, given the potential for shifts in production and end-of-life impacts, the GHG emissions associated with a business-as-usual scenario could vary significantly. For example, Zheng and Suh [9] and Stegmann et al. [41] predict that the global waste management of plastics will shift more towards incineration, leading to a carbon footprint of roughly 6.5 Gt and 3.8 Gt CO_{2e} in 2050, respectively. Zheng and Suh further show that even if the carbon footprint of the global electricity grid reaches net-zero by 2050, the emissions from the plastic sector could still amount to roughly 3.2Gt under their predominantly incineration-based waste scenario. Therefore, despite the uncertainty in future plastic production, the conservative “business-as-usual” estimate used herein highlights the potential for significant GHG savings of up to 6.5 Gt under a bio-based plastic scenario.

4. Discussion

In this study, we find that globally, a minimum of 40% recycling, 70% renewable energy, or 60% bio-based plastics needs to be achieved to reach net-GHG-negative emissions. Further, we see that a combination of strategies, such as 47% recycling, 100% renewable energy, and 80% bio-based plastics, could lead to the plastics industry acting as a carbon sink by 2040. Some regions such as the United States and Europe, have stated goals for the plastic industry that align with the targets set forth in this roadmap. However, most plastic growth is expected to occur in emerging economies in Africa and Asia. Similarly, the mass of plastic waste is expected to grow most rapidly in countries with less developed waste management systems [8]. Therefore, policies enacted at the regional level are not sufficient. Rather, like all climate change mitigation strategies, a united approach which enables developing economies to take part in the transition to

a more circular, bio-based plastic economy is needed. Currently, the UN is developing an international legally binding agreement to help minimize plastic pollution [354]; however, a holistic assessment of both the production and end-of-life impacts of plastics is necessary to achieve climate change mitigation goals.

It is also important to consider the costs and energy demand associated with the transition to a circular, bio-based plastic economy. Although the production of bio-based plastics may result in significant energy demands due to additional pretreatment and processing steps required for the conversion of feedstocks [355], the increased rates of recycling could help drive down energy demand. Stegmann et al., found that a 30% reduction in final energy use, compared to a business as usual scenario, by 2050 could be achieved with a recycling rate of more than 70% [41].

Despite the relatively high capital costs of large-scale bio-based plastic production and chemical recycling, continuing to rely on fossil resources and the need to implement carbon capture and storage to meet climate change mitigation goals would lead to overall higher costs compared to the proposed herein circular, bio-economy scenario [42]. Further, we note the life cycle inventory data used in this work often relies on lab-scale data for energy consumption and chemical inputs. When these lab-scale processes are optimized for efficiency by improving product yields and chemical recovery, the cradle-to-gate impacts of some bio-based plastics have been found to decrease by 91-97% [356]. Therefore, it is important to consider the impacts of scaling production on expected emissions, as this could enable the bio-based plastic market to generate an even larger carbon sink and reduced final energy demand relative to results we present. Further, the continued use of fossil-based plastics also has associated costs to society as

a result of climate-change induced disasters, which would further emphasize the economic favorability of shifting to a circular bio-based plastic economy [40].

Although some roadmaps exist for the petrochemical sector as a whole [7,357], a detailed pathway forward for the plastic sector that acknowledges technology readiness levels and resource availability has not yet been highlighted. Of the plastic roadmaps that do exist, they are often based on aggregated data rather than a bottom-up approach, and rely on the incorporation of carbon capture, and reduced plastic demand [358]. Therefore, this work serves as a pivotal step for further investigation of the future of the plastic industry by presenting technological solutions that could be implemented in the short, medium, and long-term using solely bio-based resources, modifications to end-of-life treatment, and renewable energy. This work can also help policy makers navigate the path to net-zero plastics by providing an understanding of what targets (such as a minimum of 40% recycling, 60% bio-based plastics, or 70% renewable energy) need to be met, and which targets (such as biodegradable plastic waste management) have more flexibility. This is vital given the urgency for necessary change within the plastic sector and the many roadblocks that exist in achieving a net-zero emissions by 2050.

This study utilizes a bottom-up LCA approach, and some technologies were not considered due to limited data availability. Therefore, future work could be expanded to examine novel bio-based plastics such as bio-based TPS blends (e.g. TPS/PLA), and fully bio-based or iso-cyanate free PUR plastic [359]. In addition, the use of CO₂ from flue gas from other industries as a feedstock for plastics, often seen as a solution to the hard-to-abate industrial GHG emissions, could be extremely valuable not only from a CO₂-removal perspective but also from a resource

conservation perspective, opening up the use of biomass residues for other applications. Another factor that is important to consider is the make-up of the plastic market. In this study, the market share of plastics by type was assumed to remain constant. However, it is possible that the make-up of the plastic market will shift with the introduction of bio-based plastic. Increasing the share of biodegradable plastics, for example, could lead to more end-of-life GHG emissions compared to non-biodegradable materials which can impact the overall CDR potential. Therefore, future research should incorporate economic models to investigate how shifts in the plastic market may impact overall results. Finally, in this study, only GHG emissions are examined, but it is important to consider in future analysis the multitude of other environmental impacts that arise from agricultural processes such as eutrophication, acidification, water consumption and land-use change [34].

4.1. Sensitivity to chemical recycling methods

Chemical recycling methods need to be leveraged to reach global recycling targets. However, given the lack of large-scale data availability for chemical recycling processes, and the sensitivity of impacts based on the plastic feedstock stream, we conduct a sensitivity analysis to examine how a change in the impacts of chemical recycling via pyrolysis may impact results. We find that when using data published by Xayachak *et al.*[360], treating 30% of plastics via chemical recycling in 2050 would lead to an annual carbon sink of 0.5 Mt, a nearly 100% reduction in CO_{2e} storage compared to the baseline scenario (presented in figure 2) using data from Jeswani *et al.* (See Appendix C, Supplementary Data 7 for detailed inventories and results). Differences in results between these two pyrolysis processes can be partially explained by having different life cycle inventory sources (Jeswani *et al.* use data from a technology developer,

whereas Xayachak *et al.* used an average from data collected in literature), as well as differences in plastic feedstock stream (Jeswani et al., model pyrolysis using a feedstock mix of PE, PP and PS, while Xayachak *et al.* use an equal mix of PP, HDPE and LDPE). Additional chemical recycling methods such as hydrolysis, glycolysis and hydrogenolysis were also examined and found to have environmental impacts of 7-18 kg CO₂e/kg (or 2-5 kg CO₂e/kg when using renewable energy) [361]. Therefore, without accounting for the avoided burdens of virgin plastic production, these end-of-life methods results in greater GHG emissions than incineration. These high environmental impacts are partially due to limitations of lab-scale studies, which are often not optimized for efficiency [362]. These results highlight the need for a better understanding of the sensitivity of the global carbon footprint of plastics to various chemical recycling technologies. Further, LCA studies of chemical recycling pathways should report results without the application of credits given that the credits will not apply if we shift towards a bio-based plastic economy (e.g. applying a carbon credit for chemically recycling PET for avoiding the production of fossil-based ethylene glycol will not be applicable when ethylene glycol becomes bio-based

Chapter 5. Carbon storage potential beyond plastics materials

Authors note: This work is a compilation of two pending publications. “Construction materials could theoretically sequester half of global CO₂ emissions” which is anticipated to be submitted to *Science* by 6/4/2024 and “A lifecycle framework for carbon uptake in the built environment” which is anticipated to be submitted to *Environmental Science and Technology* by 5/3/2024.

Abstract

Achieving net-zero greenhouse gas (GHG) emissions – i.e., balancing the amount of GHG emissions humans produce with an equal amount we can remove from the atmosphere – will entail not only lowering emissions but also developing carbon dioxide removal (CDR) technologies. Here we explore the scale of CO₂ that might be stored annually in consumed construction materials, including concrete, brick, asphalt, wood, and plastics. We find that fully replacing these conventional materials with CO₂-storing alternatives could sequester 19.3 Gt of CO₂ each year, which is roughly 50% of anthropogenic CO₂ emissions emitted in 2021. We find that the total CDR potential is driven by the level of implementation (e.g., how much material is used as a CDR technology) rather than the degree of uptake for a given unit mass of material. Given the prodigious demand for construction materials worldwide, such materials could thus be a critical opportunity for removing carbon dioxide from the atmosphere at climate-relevant scales. To drive further investigation of CDR in materials, this work presents a framework to analyze full lifecycle emissions of a building material and determine the carbon sequestration potential utilizing a time-dependent global warming calculation. This framework allows for consistent comparisons across materials and emissions mitigation strategies at varying lifecycle stages and can be adapted to calculate net uptake and sequestration potential for other materials with different lifespans and applications. The flexibility of this method, and the ability to identify GHG emission hot-spot lifecycle stages, will be instrumental in identifying pathways to

achieving net-carbon-sequestering building materials. Furthermore, given that the global assessment of CDR in plastics presented in this dissertation focuses solely on emissions occurring within one year, this tool can be integrated in future work to better understand the impacts of dynamic emissions within the plastic industry.

1. Introduction

Achieving removal of carbon dioxide (CDR) or other GHGs from the atmosphere requires mechanisms for both capture and storage of atmospheric carbon, and the most frequently discussed storage option is underground in geologic reservoirs, such as porous rock or salt caverns. However, as highlighted by the National Academies of Science, Engineering, and Medicine, value-added products are another promising option for storing large quantities of carbon [363]. In particular, building materials offer two characteristics that make them uniquely well-suited to act as a means for CDR: (a) their quantity – over the last 100 years, the total mass of infrastructure materials was nearly as high as that of all human food, animal feed, and energy resources combined [364]; and (b) their longevity – structural materials typically remain in use for decades, which can contribute to their sequestering GHGs on a long enough time horizon to contribute to climate benefits [365]. These two factors combine to make this enormous human-made mass of materials an immense opportunity to uptake and store GHGs [366]. Further, engineering this class of materials to act as a CDR method is a logical first step given the large mass of materials already consumed in the built environment, eliminating the need to develop and scale entirely new industries for CDR.

Although there are now available and feasible options for generating emissions-free electricity and electrifying transportation and buildings [2], the near-term potential for reducing emissions

related to structural materials is more limited [367–369]. This limitation arises in large part from GHG emissions stemming from currently unavoidable chemical reactions occurring during the production process [370]. For example, the majority (~60%) of emissions from cement production result from limestone decarbonation, while steam cracking and reforming of petroleum feedstocks contribute to roughly 30% of plastic production-related CO₂ emissions [371]. Altering production of structural materials to both drastically reduce process emissions and store carbon could thus help to meet both emissions reduction and carbon removal targets. Here we examine the global potential to store carbon in the most common construction materials: concrete, brick, asphalt, plastic, and wood. These materials make up the majority (~88%) of the 36 Gt of construction-related annual material consumption in 2016 [372]. In recent years, the production of building materials has resulted in an estimated 3.5-11 Gt of CO_{2e} or 10-23 % of global GHG emissions [373–375]. Excluding energy-related emissions (for which there are distinct mitigation options), the process emissions from producing the construction materials examined herein accounted for ~1.8 Gt of CO₂ emissions in 2016, or ~5% of global CO₂ emissions [6,376]. However, not included in this estimate is the biogenic carbon stored in wood products in 2016, which amounted to ~2.3 Gt of CO₂ (assuming atmospheric CO₂ removal occurred on an equivalent time horizon to wood production, which could be the case with sustainable and continuous forestry practices).

Recent studies have explored the application of new technologies to alter the composition and manufacturing methods of structural materials to facilitate uptake of CO₂ or CH₄ by the materials or their constituents, and thereby reversing some or most of the process emissions [365]. Similarly, the uptake of GHGs during use and end-of-life of these materials have also been

considered, but such uptake occurs slowly over decades [377]. Here, we calculate annual CDR potential of construction materials assuming 2016 levels of consumption (as this is the most recent year with available consumption data for all building materials), all carbon within materials (stoichiometric or measured) originated from the atmosphere, and the storage is effectively permanent (details of our analytic approach are presented in Appendix C). In summary, we estimate the CO₂-storing capability of various construction materials. These estimates are based on the extent to which conventional inputs could be substituted by alternatives that either contain biogenic carbon (e.g., recently removed from the atmosphere via photosynthesis) [46,378] or contain key minerals (e.g., recently formed carbonate minerals that may solidify with the use of concentrated sources of CO₂) [379]. In each case, we consider the materials' composition and compare uptake with related process emissions of the materials' conventional alternatives. Note, we assume that building materials, such as those examined in this study, have negligible use-phase emissions and uptake (e.g., excluding emissions from maintenance and CO₂-uptake resulting from concrete carbonation), and we assume these materials are likely landfilled at end-of-life resulting in minimal GHG emissions [380]. However, given that the end-of-life stage, particularly for bio-based materials, can result in significant emissions (e.g., methane emissions from anaerobic biodegradation), we also provide a tool for calculating the carbon storage potential of a material that accounts for the timing of emissions fluxes during all lifecycle stages. Traditional global warming potential calculation methods, such as GWP100, work by simply summing emissions together for the lifecycle of a product, assuming they all occur at the same time. However, given the long use-phase for some materials, emissions occurring during production and end-of-life can occur on very different time horizons and therefore have different impacts on cumulative radiative forcing (CRF). Herein, we

provide a tool which takes time sensitive GHG fluxes that occur throughout a material's lifecycle as inputs to determine the carbon uptake and storage potential. Further, the outputs of the tool include a detailed breakdown of the contribution of each lifecycle stage to total cumulative radiative forcing to identify hotspots and drive further emissions reductions.

2. Methods

To determine the CDR potential of these building materials, their carbon content was determined (Appendix D, Supplemental Data 3). Specific assumptions for each group of materials are outlined in the following subsections.

2.1. Theoretical storage potential per material

Cements. We assume that conventional Portland cement can be replaced with two carbonatable cements, carbonatable calcium silicate clinkers (CCSC) and magnesium oxides derived from magnesium silicates (MOMS). Through carbon mineralization, CCSC and MOMS are theoretically capable of sequestering roughly 0.2 and 0.5 kg CO₂/ kg cement respectively [379]. We note, there are technical limitations for these cements that may accrue at later life cycle stages: the pH of CO₂-cured cements is not high enough to protect steel from corrosion in reinforced concrete applications; the long-term durability of carbonatable cements requires further investigation prior to use; resource availability for CCSC is limited in many regions; an energy-efficient method for extracting MgO from relatively abundant magnesium silicate rocks has not yet been identified. Shifts in performance must be addressed and properly accounted for prior to utilization to ensure appropriate application.

Aggregates. We assume that traditional aggregates could be fully replaced with carbonate-based aggregate. Aggregates constitute the majority of concrete by mass, and sedimentary rocks are most typically used. We consider the use of synthetic rocks that have been formed via enhanced weathering to create pathways for accelerated carbon-uptake from the atmosphere, often resulting in materials with similar composition to the sedimentary rocks that are conventionally used [381]. Although such carbonate-based aggregates are at varying technology readiness levels, we consistently model the CO₂ uptake potential based on the mass fraction of carbon in two carbonate minerals: CaCO₃ and MgCO₃. Based on the molecular masses of Ca, Mg, C, and O, we can estimate that carbon content is approximately 12% to 14% for aggregates. However, the most common means of extracting MgO and CaO that could then react with CO₂ under proper conditions to form CaCO₃ and MgCO₃ currently rely on decarbonation processes, which would lead to equivalent or greater emissions than the uptake potential (i.e. net emissions not net removal). However, other pathways exist, including mixing Mg- and Ca-rich industrial waste with a carbonate slurry (typically made from concentrated sources of CO₂ to achieve sufficient reaction times) to generate carbonate-based aggregates, thereby simultaneously valorizing waste materials and sequestering atmospheric CO₂ [382]. Similarly, crushed concrete contains calcium hydroxide, which can react with CO₂ to form calcium carbonate ($\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$) under appropriate conditions. Yet industrial wastes are currently not managed effectively, with roughly 50% of concrete waste going to landfills [383].

Biochar additives. While biogenic resources cannot easily be used at high levels within highly alkaline concrete, low levels of biogenic additives, particularly if they have undergone processing that improves dimensional stability and resilience in higher alkalinity, can act as a

means of storing CO₂. Using biochar to store carbon in this way can valorize waste products such as agricultural byproducts. The carbon content of biochar can vary significantly based on the type of feedstock, therefore a ranges of 0.3 to 0.85 kg C / kg biochar [384,385] is used. We analyze the potential if cement were replaced with up to 15 wt% of biochar, but note that replacement levels >5 wt% can lead to reductions in mechanical performance characteristics such as compressive strength [386], depending on characteristics of the biochar. Therefore, high levels of biochar replacement in concrete may only be possible for low load-bearing applications or when the biochar has desired properties.

Wood. Current use of wood as a building material accounts for roughly 2.2 Gt of stored CO₂. In addition to this photosynthetic carbon already being stored in the built environment, here we consider the effects of an increase in wood consumption by up to 20 wt% given that the demand for industrial roundwood is expected to increase 25-40% by 2050 [387]. Wood carbon content is variable depending on parameters such as species; however, most wood has a carbon content in the 40-60% weight range [388]. While wood has been examined for its potential to store carbon in the built environment [389], we limit the degree to which it can be scaled to store carbon based on the complexities associated with resource availability, forest management, end-of-life management, and land-use changes, among others [390], as well as the inability to use wood for many building material applications (e.g., roads, foundations). Further, we note that carbon accounting schemes, and land-use change assumptions, could lead to varying outputs for wood resources [390]; herein, we quantify the potential CO₂ stored in a single year time horizon, we do not account for losses due to soil disturbances, and we assume forestry management practices that support continuous carbon storage – the potential of which has been debated.

Bio-based Plastics. Plastics are not a large mass fraction of the built environment relative to materials like concrete and wood, but their use is gaining popularity, and pathways for creating carbon-storing plastics have been proposed. Consistent with other modeling assumptions, we calculate the CDR potential of plastics based on the mass fraction of carbon in the polymer, and this carbon is derived from atmospheric CO₂ via photosynthesis of biomass. The storage potential of bioplastics is sensitive to the type and source of biomass feedstock used given implications for land-use change emissions [34,391], which are outside the scope of our analysis. Plastic carbon content is also variable depending on backbone composition, additives, and other parameters, therefore a range of 40-90% is used. We also note that bio-based plastics now make-up ~1% of the plastic market, most of which are biodegradable and therefore not suitable for construction applications [21]. Although production processes for more durable, nonbiodegradable bio-based plastics exist on a commercial scale, production costs are relatively high compared to fossil-based plastics which has limited their growth rate, with only 0.2% of bioplastics being used in construction applications [21].

Brick. Brick, the oldest artificial building material, remains important, with roughly 1.2 trillion bricks produced annually [392]. Recent studies have examined the potential for using agricultural wastes in brick [393]. In this study, we assume up to 15 wt% of brick can be substituted with biomass fibers, a ratio which has been shown to maintain similar performance characteristics as traditional brick materials [394,395]. The carbon content of biomass fibers can vary significantly based on the type of feedstock, therefore a range of 0.4 to 0.6 kg C/kg [396] is used. We assume the remaining mass (85%) of brick is calcium carbonate formed via complete

mineral carbonation of portlandite ($\text{Ca}(\text{OH})_2$), which results in CDR, similar to the processes described for crushed concrete. It is important to note that although portlandite is a naturally occurring mineral, it is not abundant enough to meet the current demand of brick production. Therefore, similar to carbonatable cements, energy-efficient production pathways still need to be identified for this class of materials. Although studies have examined the mechanical performance of portlandite brick, further research should investigate the mechanical performance of calcium carbonate brick, as well as the time scale required for complete carbonation.

Asphalt. Similar to concrete, asphalt pavement is a composite material that can be formed with several different carbon-storing materials. Here we consider the effects of using a carbon-storing binder and aggregates. We assume up to 100% replacement of traditional aggregate in asphalt pavement, with carbonate-based aggregate, with the aggregate uptake methods discussed above.

Bio-oil for asphalt. Asphalt pavement has two main components: (1) aggregate, which makes up roughly 95 wt% of asphalt, and (2) binder, asphalt bitumen, responsible for holding the aggregate together. Asphalt bitumen is typically made from petroleum refining residues. Here we model the replacement of petroleum bitumen binders with bio-oil, a byproduct obtained from the thermal decomposition of biomass through pyrolysis or hydrothermal liquefaction. Due to the similar chemical and rheological properties of bio-oil and asphalt binder, bio-oil can be used as a substitute or modifier for traditional fossil-based asphalt binder. In addition to serving as a carbon storage method, the use of bio-oil instead of fossil-based asphalt has been found to reduce energy requirements and costs due to lower required production temperatures [397]. The carbon content and performance characteristics of bio-oil can vary depending on its source [398]. Here,

as was done with our bio-based plastics models, CO₂ storage potential is based on carbon content. The carbon content of bio-oil for use in asphalt bitumen varies depending on the source, therefore literature on bio-oil production from agricultural by-products [399], wood waste [400], and food waste [401], was leveraged to obtain a range of carbon content (0.3 to 0.7 kg C/kg). We note, as with several of these CDR technologies, there are currently reported performance differences from this biogenic resource. In general, it has been observed that the addition of bio-oil improves anti-aging and low-temperature performance but compromises high-temperature performance compared to traditional asphalt binder.

2.2. Method of calculation

For woods, plastics, aggregates, and bricks, stoichiometric relationships were used to determine the CDR potential. Namely, the following relationship was applied:

$$\text{mass of CO}_2 \text{ stored} = \text{carbon content} \times 44/12 \quad \text{S1}$$

The ratio of 44:12 is based on molecular masses of CO₂ and C respectively. We do not reflect additional emissions from the processes performed. We note the majority of processes require energy resources that have associated greenhouse gas (GHG) emissions. However, to estimate the CDR potential of building materials, we draw comparisons to the chemical-derived emissions of conventional materials. Using storage capacity, our findings suggest energy-derived emissions can still occur from the production of these CDR materials and still meet desired 1.5°C and 2°C warming targets with appropriate implementation of strategies.

Because conventional cement has minimal carbon content, we model three permutations on cementitious materials in this work. The first is based on a CCSC, for which the CDR potential

has been modeled as 0.216 kg of CO₂ / kg of cement in previous work [402]. The second is based on the carbonation of MOMS. In this second case, the CDR of 0.524 kg of CO₂ / kg of cement is modeled based on previous work [402]. Finally, we consider the scenario in which 15% of cement is replaced by a high carbon content filler, such as biochar. In this third case, cement CDR potential is reduced by 15% and replaced by an 85% carbon-content biochar; the uptake potential of this biochar is determined following equation S1.

3. Results

3.1 The carbon storage potential of our built environment

The schematic in **Figure 12** shows the relevant capture mechanisms and magnitude of CDR per unit of different construction materials. Several key takeaways are highlighted in this diagram. While bio-based plastics resulted in the highest CDR potential per kg of material, they contribute the least to total CDR potential due to the relatively small production quantities compared to all other building materials. Inversely, aggregates in concrete have one of the lowest (<1 kg CO₂/kg) CDR potentials; yet, due to the substantial scale of global demand, they present the largest CDR potential. Considering these tradeoffs, areas ripe for rapid market penetration and potential for mass scaling could lead to more substantial climate benefits than driving the greatest degree of uptake for any individual CDR option.

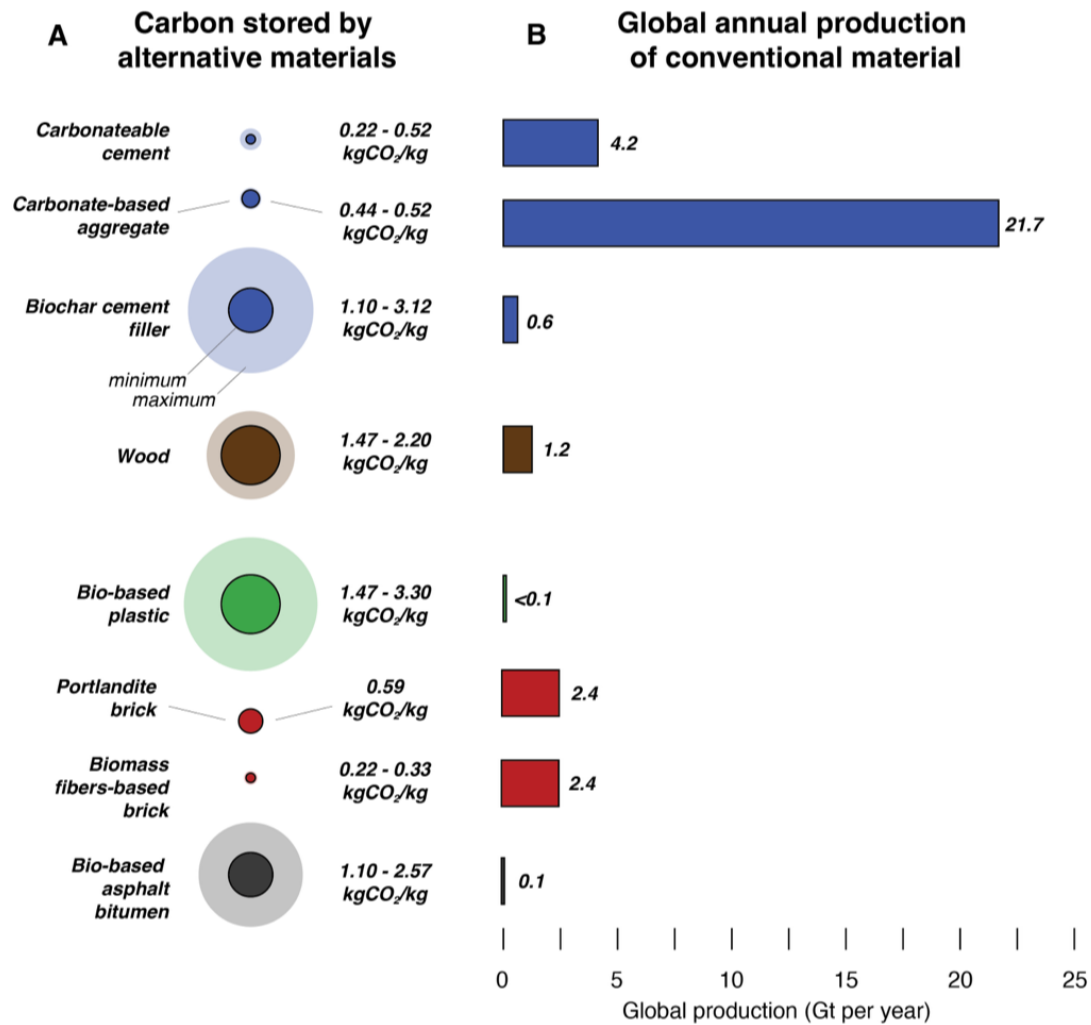


Figure 12. The potential to store carbon in construction materials varies considerably depending on the carbon density of alternative materials (kg CO₂ per kg material, A) and the scale at which conventional materials are being used (B).

Our results show if all the alternatives we consider were applied simultaneously, the built environment could sequester 13.8 to 19.3 Gt of CO₂ each year, assuming minimum and maximum carbon contents, respectively. Meanwhile, process emissions from the production of these materials were approximately 1.8 Gt of CO₂ in 2016 (i.e., excluding energy-related emissions), so the combined mitigation opportunity of avoiding process emissions and storing carbon is >20 Gt CO₂ (Table 7), which is equivalent to roughly 50% of CO₂ emitted from all anthropogenic sources in 2021 [403]. Most of this storage, ~12.5 Gt of CO₂, is attributed to

aggregates used in concrete and asphalt pavement. This notable capacity for fixed carbon is driven by the large mass of aggregates used in these two materials, which outweigh the other materials by three-fold. Noting different permutations were considered for CO₂ storage in cement, we find that the combination of a magnesium-oxide based cement, synthesized from forsterite and carbonated, with 15 wt% biochar as filler results in the highest level of CO₂ capture (~ 0.9 kg of CO₂ absorbed per kg of cementing binder), resulting in a total potential storage of 3.7 Gt CO₂. Bricks were the next most significant material for CO₂ storage, and by assuming a biomass fiber carbon content of 0.6 kg C/kg, the global production of bricks can result in roughly 0.8 Gt of CO₂ storage. This quantity of storage is equivalent to 1/3 of the mass of bricks produced, despite fibers comprising only 15 wt% of the brick. Additionally, mineral carbonation of portlandite in bricks can lead to an additional 1.2 Gt of fixed CO₂. If the market and appropriate forestry practices can support increasing wood consumption by 20%, an additional 0.5 Gt of CO₂ can be absorbed. Our findings also show an additional degree of CO₂ storage (<5%) can be attributed to bio-based plastic and asphalt binder, with storage potential resulting from relatively low consumption (less than 0.2 Gt).

Table 7. Summary of the global carbon dioxide removal potential of the materials examined based on 2016 global production values and using average values for carbon content. Chemical-derived emissions for traditional materials are presented as well for reference.

<i>Material</i>	Global material production (Gt)	Global chemical-related emissions (Gt CO₂)	Global carbon dioxide removal potential (Gt CO₂)
<i>Concrete aggregate</i>	21.7	0	-11.4
<i>Asphalt aggregate</i>	2.1	0	-1.1
<i>Cement</i>	4.2	1.7	-1.8
<i>Cement filler</i>	0.6	0	-1.9
<i>Brick</i>	2.4	0	-2.0
<i>Wood</i>	1.2	-2.3	-0.5
<i>Asphalt bitumen</i>	0.1	0	-0.3
<i>Plastic</i>	0.1	0.1	-0.2
Total	32.4	-0.5	-19.3

Noting the wide range of potential CDR scenarios, we conduct a sensitivity analysis to address the impact of carbon-content modeling assumptions as well as varying the level of implementation on the total sequestration potential (**Figure 13**). Findings solidify that the single largest driver in CDR is the mass of resources consumed, with aggregate and cement for concrete production having the highest consumption (**Figure 13a** and **Figure 13b**, respectively), followed by brick and asphalt aggregate. The modeled carbon content of these materials also contributes to their CDR potential, where higher carbon content drives greater CDR potential, but this parameter is notably outweighed by material demand in terms of total CDR.

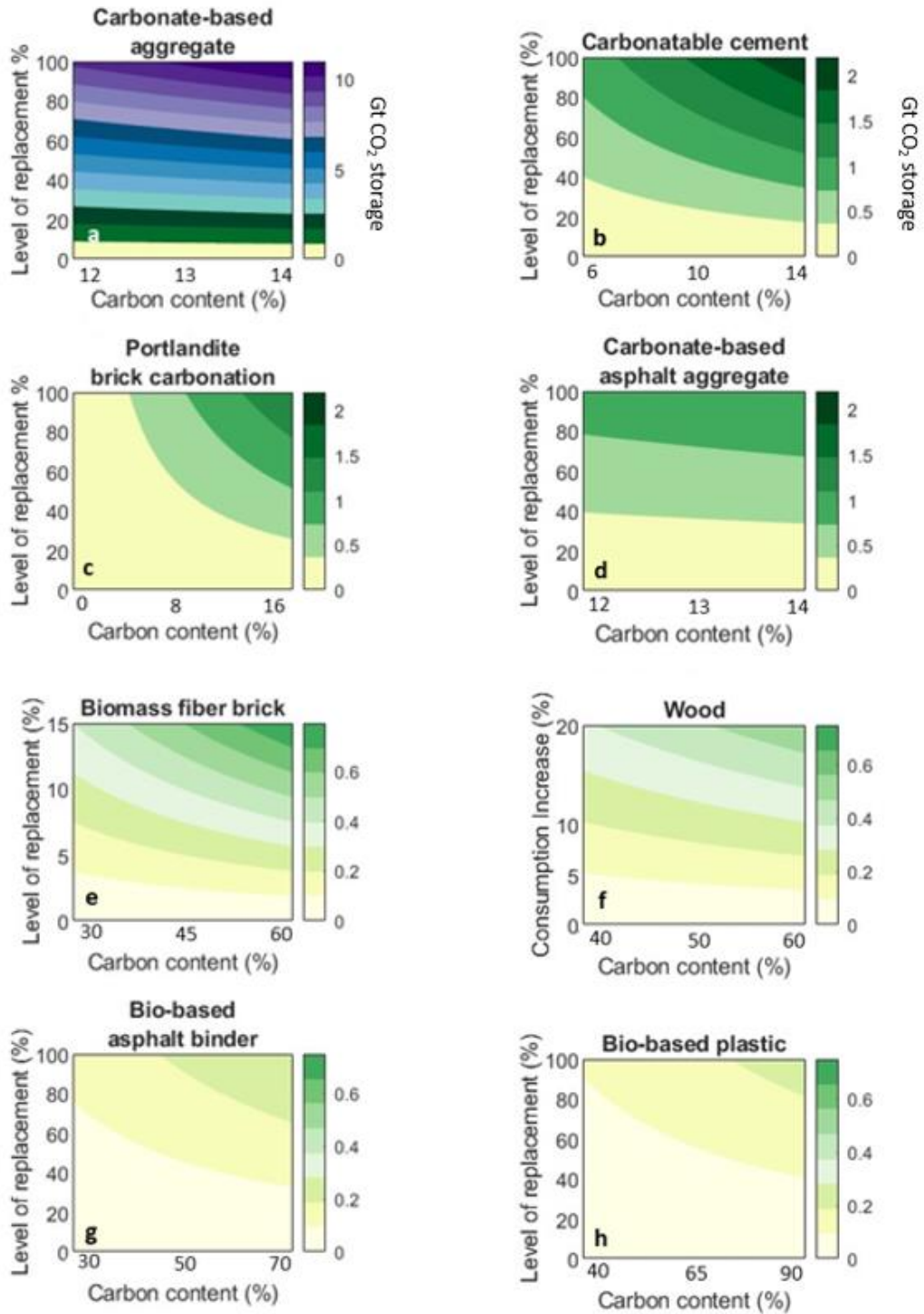


Figure 13. Sensitivity of the theoretical carbon uptake potential for each material to carbon content and level of implementation.

3.2 Resource availability assessment

Considering the large material demand for construction and that this substantial mass of resources is the primary driver in storage potential, we conduct a preliminary assessment of resource availability to realize the described carbon storage potential. For carbon mineralization pathways, various Ca and Mg-rich industrial waste materials (namely, red mud, blast furnace slag, steel slag, mine tailings, cement kiln dust, biomass ash, lignite ash and coal ash) and end-of-life concrete are considered as potential feedstocks for carbonate-based aggregate production. Based on their annual production and elemental composition, it is found that roughly 2 Gt of carbonate-based aggregate can be produced per year, offering 1 Gt of annual CO₂ storage. Yet further exploration is being conducted on the use of resources, such as basalt for magnesium and calcium resources. If substitutions of 15 wt% of bricks with biomass fibers, all asphalt bitumen with bio-oil, and all plastics with bio-based plastics were to occur, demands would only require 5% of annual agricultural residue production (i.e., biomass resources from agricultural cultivation that are not directly used for human food). Remaining agricultural residues could be used in the form of biochar as a filler to replace 15 wt% of cement, which alone would utilize another 24% of agricultural residues, and implementing all biomass strategies considered would leave 71% of agricultural byproducts for other applications. Notably, the process of producing biochar via pyrolysis would co-produce valuable byproducts, such as syngas and bio-oil. However, we note the current production and use of biochar is currently very limited - in 2021 roughly 0.4 Mt of biochar was produced, much less than the 600 Mt of biochar that would be required for this CDR mechanism [404]. These estimates of resource demand are based on an assumption of a 1:1 carbon replacement ratio, where the carbon content of biomass is efficiently converted to the carbon content of building materials. Any inefficiencies that result in material

waste would increase material demand (a sensitivity analysis accounting for such inefficiencies is presented in Appendix D, Supplemental Data 6).

3.3 Contribution to CDR targets in mitigation scenarios

Notably, the CDR potential of the construction materials assessed exceeds the magnitude of global fossil fuel and industry CO₂ emissions that do not have readily available decarbonization pathways [2]. According to the IPCC AR6, to stay below 1.5°C and 2°C targets by 2100, a cumulative maximum of 660 Gt and 290 Gt of CO₂ would need to be removed by CDR technologies, respectively [1]. Although increases in global population and affluence are likely to drive an increase in materials production [405], we make a conservative estimate that the overall quantities of different building materials remain at 2016 levels in the future. With this magnitude of materials, a full transition to these alternatives by 2025, 2050, or 2075 would allow for over 1380, 920, and 460 Gt of CO₂ to be removed by 2100, respectively (**Figure 14**). This quantity of CDR, which exceeds the required targets for staying below 1.5 and 2°C, is notable given that novel techniques for production may require more energy than traditional production (e.g., [406]). Thus, while energy-related emissions were not directly modeled in this work, these findings suggest that some energy-related emissions associated with the conversion of construction materials to CDR mechanisms on these time horizons could still occur without inhibiting the ability to achieve desired emissions reduction targets.

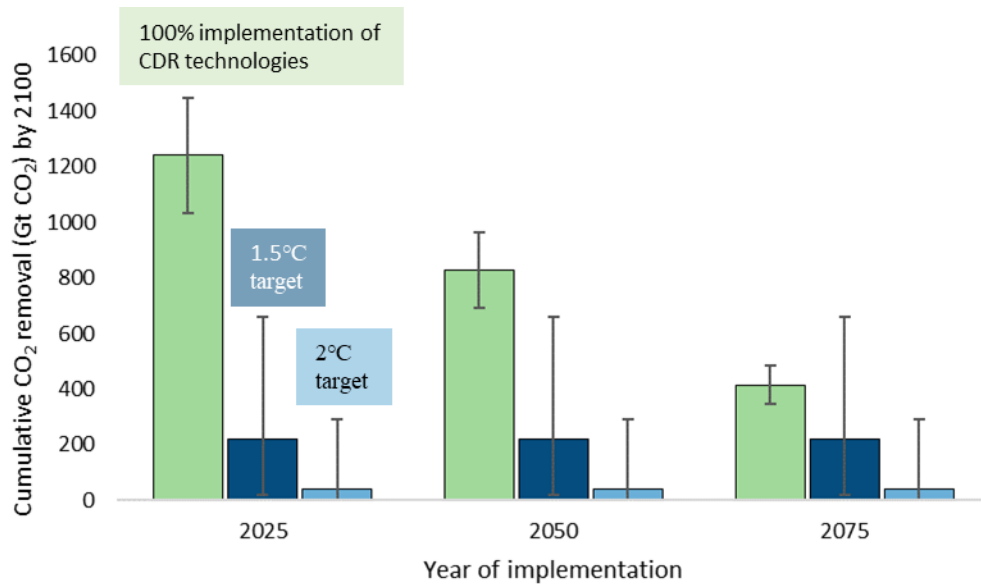


Figure 14. Cumulative CO₂ removals by 2100 as a function of the year of implementation of CDR technologies. Cumulative CDR is compared to the required targets for the IPCC 1.5°C (dark blue) (a) and 2°C (light blue) (b), assuming full implementation of the technologies presented herein. The error bars represent the minimum and maximum values for CDR removal.

In addition to energy-related emissions, resource constraints may also be a limiting factor to achieving CDR requirements in mitigation scenarios. Therefore, an additional assessment was conducted to analyze the potential for using only currently available resources: namely, replacing roughly 10% of aggregate with carbonate-based aggregate, substituting 15% of brick with biomass fiber, fully transitioning to bio-based plastic production, utilizing bio-oil based asphalt binder, and replacing 6-15% of cement with biochar filler. We find that fully implementing these technologies by 2045 and 2090 would be sufficient to achieving the median targets for 1.5 and 2°C scenarios, respectively (**Table 8**).

Table 8. Assessment of resource availability constraints on the ability to meet IPCC climate change targets of 1.5 and 2°C.

Global warming target with limited or no overshoot	Total cumulative CDR deployment necessary (Gt CO ₂)	Take-off year required to achieve cumulative CDR target	
		Scenario 1: Using all currently available resources	Scenario 2: Using all currently available resources but not counting increase in wood consumption
1.5°C	Min	20	2095
	Median	220	2045
	Max	660	1935
2°C	min	0	n/a
	median	40	2090
	max	290	2027

While these resources are technically available for use in buildings as CDR mechanisms, it is crucial to recognize their potential suitability for other applications outside of building materials, such as energy production or animal feed. Namely, biochar generation was calculated assuming yields associated with slow pyrolysis; however, it is possible that other biomass processing methods such as gasification are utilized which could influence the quantity and quality of biochar generated. Similarly, mineral wastes such as blast furnace slag are increasingly implemented as supplementary cementitious materials (SCMs), limiting their availability for use as carbonate-based aggregates. Furthermore, shifts in demands of these resources may result in unintended consequences (e.g. indirect land-use change impacts resulting from increased biomass consumption). Therefore, efforts to derive sustainable cultivation practices and materials production pathways, proper accounting of GHG fluxes and other environmental impacts beyond climate damages must be addressed in new research efforts.

3.4. Accounting for dynamic emissions with a carbon storage assessment tool

Given that the assessment conducted herein on the carbon storage potential of materials is limited to determining the static, theoretical carbon uptake occurring during production of materials, without consideration of end-of-life emissions, we provide a tool for comprehensively assessing the carbon storage capacity of various materials based on full lifecycle data that accounts for the timing of emissions uptake and release (see attached supplemental excel file). Furthermore, given that the global assessment of CDR in plastics presented in this dissertation focuses solely on emissions occurring within one year, this tool can be integrated in future work to better understand the impacts of dynamic emissions within the plastic industry.

3.4.1 Requisite inputs and outputs

To implement this framework for addressing dynamic GHG fluxes throughout a materials life cycle, a scope of assessment and inventory of GHG fluxes are needed. While all GHGs can be addressed using this framework, we present an implementation of the method derived in a simplified calculator in the Supplementary Materials (Appendix D). This calculation method facilitates three primary types of inputs: (1) the CO₂, CH₄, and N₂O emissions associated with each life cycle stage in units of kg gas/unit product; (2) the CO₂ uptake associated with each life cycle stage in units of kg gas/unit product; and (3) the duration of specific life cycle stages, namely raw material acquisition (e.g., rate of photosynthetic carbon uptake in biomass), use/maintenance (e.g., the length of time the product is in service), and EoL (i.e., the time horizon over which end-of-life fluxes are anticipated to occur, such as material decay). CO₂, CH₄, and N₂O emissions have been reported as the most prevalent GHG emissions from building

materials production, [407] and therefore we focus on these gases. The calculator assumes that manufacturing/assembly, transportation from raw material acquisition to construction, and construction cumulatively occur within one year and that removal/demolition and transportation to waste treatment together occur within one year.

To use this calculator, a user must determine several key factors. First, for the material or product of interest, define a scope of analysis. This scope should include factors such as anticipated shifts in material use (e.g., demand for repair), potential EoL management pathways, whether a consideration for improved energy grids in the future or other material availability in the future are of interest, whether alternative production pathways (e.g., using carbon capture and storage for energy facilities, use of renewable energy resources) are of interest, and the expected time horizons for material synthesis, use, and EoL. We outline these key phases to consider while determining the scope of assessment in **Figure 15**. After a scope is determined, the user must address anticipated GHG uptake and emissions at each of the eight primary stages presented in **Figure 15**. Namely, an inventory of the CO₂, CH₄, and N₂O emissions and uptake must be determined per unit of material. These GHG fluxes must also be quantified for any permutations of interest (e.g., electricity grid mix variations). With these inputs and outputs, the methodology can be implemented.

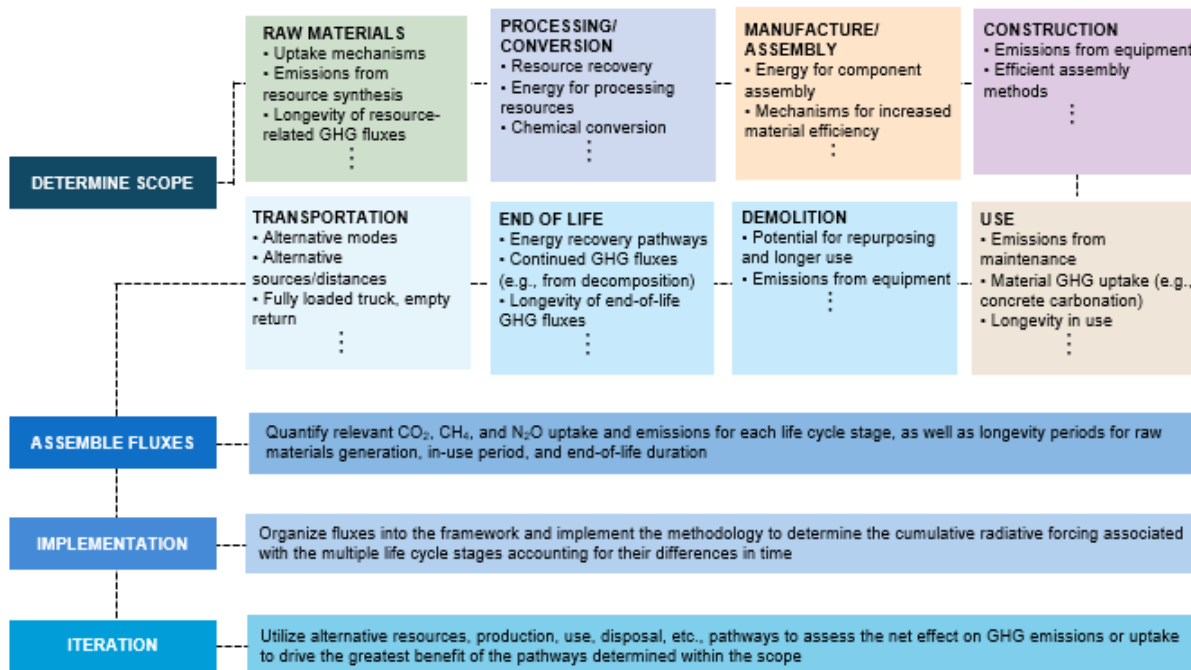


Figure 15. Data considerations to determine for the scope of assessment, greenhouse gas fluxes to consider, implementation, and iteration for the proposed method.

The outputs of this calculator provide mechanisms to assess the cradle-to-grave time-adjusted global warming potential (TAWP) of a product [408]. The tool is inherently functional unit independent and more complex material systems can be modeled if input fluxes are normalized to that specific system. Results output a traditional GWP value as well as a TAWP value. The TAWP value considers the impact of the timing of emissions and the resulting impact on cumulative radiative forcing. In addition, the calculation method provides the percent contributions of each lifecycle stage (i.e., resources, processing, manufacturing, construction, use, demolition, end-of-life, and cumulative transportation-related emissions throughout the system) to the overall TAWP. This breakdown allows users to determine hotspots of uptake and sequestration, and as a result, they can alter parameters to understand manufacturing, use, and disposal pathways that drive desired net fluxes.

3.5 Opportunities in industry and policy

Many of the carbon-negative building materials we assess have the potential to be cost-competitive with the conventional materials they replace due to the low market price of mineral waste and biomass feedstocks that are needed. As a result, an increasing number of companies are beginning to produce materials with CO₂-storing capabilities, suggesting there is market demand.

Companies working to reduce the carbon footprint of concrete have primarily focused on producing both low-carbon binding agents and synthetic aggregates. But some companies are working on the types of alternative cements we model here. For example, Solidia Technologies and Caron Upcycling UCLA are sequestering CO₂ in cement via carbon mineralization, reporting up to 70% lower CO₂ emissions than conventional concrete [409,410]. And BluePlanet and Carbon8 Systems are producing synthetic carbonate aggregates using alkaline rock and industrial wastes combined with CO₂ waste streams to create carbon-negative building materials [382,411].

Bio-based plastics have been around since the early 20th century, but only account for roughly 1% of total annual plastic production, 48% of which is used in short-term packaging applications [412]. However, the bio-based plastic market is expected to expand to more durable applications like construction, driven by policy changes and the shift towards a circular bioeconomy.

Braskem and Biovyn are companies pursuing this new market by producing bio-based polyvinyl chloride (PVC) and polyethylene (PE) [413,414]. To limit land-use impacts as the bioplastic

market continues to grow, companies like Dow and Mango Materials are using waste biomass and methane as feedstocks [415,416].

Brick manufacturers have the potential to produce carbonate-based or biomass-based bricks that capture CO₂ by utilizing waste materials. Orbix, for instance, uses carbon mineralization of calcium in steel slag combined with CO₂ to create calcium carbonate-based bricks [417]. Bio Fiber Industries is using hemp as a feedstock to make construction materials such as bricks. Just Biofiber is combining biomass (such as hemp curd) and mineralization of lime to produce carbon-negative building blocks [418].

Although the use of bio-oil in asphalt as a replacement for fossil-based bitumen is not widely commercialized, Avello Bioenergy is exploring the economic feasibility and carbon sequestration potential of their patented bioasphalt binder—which was used to pave part of the Waveland bike trail in Des Moines, Iowa in 2010 [419]. Similarly, in 2021 Avantium, a chemical company in the Netherlands, partnered with an infrastructure company Roelof, to develop the first major roadway made from lignin-based bioasphalt [420].

Despite recent advances in industry, there are still a number of roadblocks for achieving the theoretical CDR quantities presented herein. Many of the companies mentioned remain at the prototype or pilot stages of production. The barrier to large-scale production could be in part due to competitive pricing of conventional building materials and the lack of established value chains necessary for widespread implementation of these alternative technologies. For example, carbon mineralization pathways require highly concentrated CO₂ gas and feedstocks rich in MgO or

CaO. This requirement often necessitates co-locating production plants near flue-gas sources and industries generating alkaline-rich waste streams, such as steel manufacturing, to make the process economically viable [421]. Similarly, while biomass-to-polymer conversion routes have reached technological maturity, bio-based plastic manufacturers struggle to scale production due to insufficient access to biomass residues required to meet market demands for plastic. Further, those specifying use of building materials tend to be risk-averse due to factors such as the potential liabilities associated with material failure [24]. A change in material composition runs a high likelihood of altering material performance. A loss in performance could pose a safety risk if not accounted for in design, and if addressed in design, it could lead to an increased volume of material to carry the same loads and/or more frequent replacement, which in turn could contribute to environmental impacts [369]. While in theory improved performance can have an inverse effect, there are hindrances to adoption. For example despite promising research indicating comparable or superior performance of carbonation-cured building materials, they have not yet been incorporated into relevant building codes and standards, making it difficult to commercialize on a large-scale [421]. Therefore, there is a need to implement performance-based codes that allow for changes in concrete composition to help achieve large scale CDR targets, while meeting safety requirements. In cases where a loss of desired performance may be expected, research to systematically quantify durability characteristics and investigation into methods that can overcome limitations may be warranted (e.g., the use of galvanization to mitigate against steel corrosion).

Given projected increases in demand for infrastructure materials [422], valorizing carbon in the form of long-lived materials could be a priority for policymakers. The urgency of mitigating

climate damages has led to emissions-reduction pledges and regulatory frameworks in many regions and countries, including for industrial materials production (e.g., California's recent bill to reach net-zero emissions from the cement industry by 2045 [423]). These policies will drive a CDR market, and use of similar policy mechanisms for energy technologies can be adapted for carbon-storing materials to overcome material technology hurdles. For example, in the United States, investment in research and development for wind turbines, tax credits to limit cost burdens, and government-driven procurement plans overcame hesitancy in early adoption and drove wind energy to account for 31% of all new generation capacity between 2008 and 2014, with cost of wind energy per kWh falling by ~85% between 1980 to 2000 [424]. Such incentives as well as regulatory policies, such as Carbon Cap & Trade that stipulates emissions allowances based on emissions, uptake, and production, can be used in unison to drive rapid advancement and adoption of building materials that capture and/or store carbon. CDR strategies in building materials are particularly pertinent for policy makers as these materials are predominantly from regionally available resources, and some proposed pathways to decarbonization can drive local resource scarcities [425] and/or lead to increased health burdens on local populations [426]. However, they can simultaneously stimulate local economies and create jobs.

Although there is immense potential for building materials to act as carbon sinks, further development is necessary for most of the technologies that would store carbon. If novel material alternatives are used to store CO₂, these materials can behave differently from conventional materials, and resolutions to these differences must be addressed. This issue is particularly pertinent for the construction industry, which is inherently risk-averse and slow to adopt new technologies (due to low profit margins and the need to ensure structural reliability) [24]. For the

implementation of robust incentives and policies to drive carbon storage, performance-based metrics for product standards and comparisons must be developed to support the inclusion of these carbon-storing building materials. Such measures can be supported through a variety of policy mechanisms and government procurement.

4. Conclusion

The results of this study demonstrate the immense opportunity for materials in our built environment to act as a method of CDR, with the capacity to store roughly 50% of annual GHG emissions. Given the large mass of aggregates used in concrete and asphalt, carbonate-based aggregates contributed the most to global carbon storage potential. Further, the study illustrates the potential for CDR in building materials to meet and exceed the IPCC's CO₂ reduction targets; fully implementing the technologies presented herein by 2045 using currently available resources would still achieve the 1.5°C target. Industry and policy environments play pivotal roles in accelerating the adoption of these carbon-negative materials. The movement toward carbon-storing materials is gaining traction among companies and within policy frameworks that encourage the development and deployment of sustainable, low-carbon materials. This momentum could be critical in transforming the materials industry into a key player in global CDR efforts. To aid future research in properly assessing the CDR potential of materials, we provide a tool that examines the timing of emissions fluxes on cumulative radiative forcing. Further, by breaking down emissions by lifecycle stage, this framework allows for a robust understanding of current hot spots in the lifecycle of materials or processes. Furthermore, it allows for comparisons of various scenarios using consistent methodologies, which can help enable material developers, policymakers, and other stakeholders to investigate pathways toward reducing GHG emissions and drive maximum sequestration in the built environment.

Chapter 6. Conclusions

1. Summary

The ability to reach net-zero emissions by 2050 is inhibited by hard-to-decarbonize industries, such as materials production. Current process-based emissions for materials production, such as manufacturing of cement and plastic, coupled with their projected growth in consumption, result in these materials making up a significant portion of the remaining carbon budget. Therefore, alternative production pathways for these materials needs to be realized. The utilization of biomass as a resource for material production has been investigated as a method to not only reduce greenhouse gas (GHG) emissions, but to also act as a form of carbon dioxide removal (CDR). This work explores the carbon storage potential of bio-based plastics and provides pathways for transforming the plastic sector from a major carbon emitter to a carbon sink. This research examines the sensitivity of life cycle GHG emissions from bio-based plastics to various factors, including life cycle assessment modeling methodologies, feedstock production pathways, and end-of-life assumptions. Previous studies have examined the theoretical CDR potential of plastics under specific, often unattainable scenarios (e.g. 100% renewable energy, 100% recycling, and/or 100% CO₂-based plastic). In contrast, this work prioritizes currently available technologies, presenting scenarios that enable the use of bio-based resources for global plastic production while achieving CDR. A roadmap for how to achieve CDR for the plastic sector by 2050 is presented. The overall framework used to investigate the carbon storage potential of plastics is applied to other building materials, such as cement, brick, and asphalt. This broader approach reveals an initial estimate of the global carbon storage potential of the materials industry. This research also introduces an assessment tool that considers the timing of emissions and uptake to determine the carbon storage potential of a material and identifies GHG emissions

hotspots. This work serves as an important building block for policymakers and industry stakeholders as it lays out pathways to turn the materials production industry from a significant carbon source to a carbon sink, and it provides a critical foundation for future research into CDR materials development. Key findings from this work include:

- The cradle-to-gate impacts of bio-based plastics can enable CDR with renewable electricity and heat.
- The CDR potential of bio-based plastics greatly depends on the allocation method used. Mass allocation resulted in the highest impacts for 2nd generation feedstocks, with economic allocation resulting in a GWP that is 137% lower on average, due to the low market value of agricultural byproducts. Conversely, for 1st generation (e.g., edible) feedstocks, economic allocation resulted in the GWPs that are 28% higher compared to mass allocation.
- GHG emissions hotspots for bio-based plastic production, outside of energy-derived emissions, include emissions from fertilizer production/application, chemical/enzyme production, and inefficiencies in biomass-to-polymer conversion processes.
- End-of-life emissions greatly affect the overall carbon storage potential of bio-based plastics, with decomposition in and off-gassing from landfills resulting in the highest GHG emissions for biodegradable bio-based plastics due to the generation of methane in anaerobic environments.
- Due to the limited number of studies examining the biodegradation behavior of biodegradable bio-based plastics in landfill environments and the heterogeneous nature of landfills, there exists high uncertainty and variability among the predicted GHG emissions associated with this waste treatment option.

- To reach CDR plastics on a global scale, a minimum of 40% recycling (with 100% renewable energy and 90% bio-based plastic), 70% renewable energy (with 70% recycling and 80% bio-based plastic), or 60% bio-based plastics (with 100% renewable energy and 80% recycling) needs to be achieved. However, over 100,000 total combinations of strategies could lead to CDR in plastics.
- Using existing technology, a 58% reduction in GHG emissions from the plastic sector could be achieved compared to a business-as-usual approach. Additionally, with 90% bio-based plastics, 90% recycling, and 100% renewable energy, ~260 Mt of CO₂ could be removed annually by 2050.
- Harnessing the theoretical carbon storage potential of cement, asphalt, brick, plastics, and wood in the built environment could enable the removal of 19 Gt of CO₂ annually.

2. Future work

One of the ambitious goals set by the United States for biotechnology is to replace 90% of plastics with bio-based alternatives within 20 years [14]. Achieving this objective requires closing several knowledge gaps to ensure the transition is environmentally sound and economically feasible. Further, research advancements are needed to understand the technological innovations, economic instruments, and policy mechanisms required to accelerate carbon dioxide removal efforts across various materials industries.

2.1 Bio-based plastic production

While this study analyzes the GHG emissions related to bio-based plastic production, it is crucial to recognize that substituting fossil-based plastics with bio-based alternatives may introduce

other environmental challenges, such as eutrophication, ecotoxicity, and land use changes. Future research should build from the bottom-up modeling efforts in this work and others to identify plastic decarbonization strategies that also minimize adverse impacts on human health and the environment. Given the predominance of non-biodegradable bio-based plastics for durable applications, further investigation of the human health impacts and ecosystem damages of microplastic generation is an important area for future research. This research area is especially pertinent given that microplastic generation will continue to grow even if landfilling rates decline because much of the dispersion of microplastics to the environment are from the utilization of household goods, tires, and clothing. In this study, various 2nd generation feedstocks, or non-edible byproducts from agricultural processing, are considered for bio-based plastic production. However, the environmental impacts of agriculture, such as CO₂ and N₂O emissions from land use and fertilizer application, remain significant. Therefore, to reduce the impacts of a bio-based economy, alternatives to traditional fertilizer production (e.g. utilizing renewable hydrogen), and more efficient fertilizer application methods, should be investigated. To optimize carbon storage in materials production, future studies should aim to improve the efficiency of biomass conversion processes.

To aid in understanding the production impacts of materials, there is a need for consistent and transparent life cycle inventory data that is regionally and temporally relevant. Most existing datasets, including ones used within this study, are based on data representative of the United States or Europe despite Asia being the largest producer of plastics globally. Therefore, life cycle inventory data for plastic production needs to be expanded and refined to include regionally and temporally relevant data to enhance the accuracy of environmental impact assessments. This is

especially pertinent for bio-based plastics given that agricultural practices vary greatly across different regions and environments. Further, plastics contain many additives to achieve desired performance characteristics which are typically not included in life cycle inventory data. Therefore, future research should incorporate the production and use of additives in life cycle assessments (LCAs) of bio-based plastics to better represent the life cycle impacts of these materials. Moreover, given that some bio-based plastics modeled in this study are not yet commercially available, some data are based on lab-scale production routes rather than large-scale production processes. Thus, future research efforts should focus on modeling the effects of scaling production on bio-based plastic production routes, as lab-scale studies are often not optimized for efficiency.

In this study, the sensitivity of LCA results to methodological assumptions, such as allocation methods or carbon accounting, is highlighted. We see that the carbon storage potential of bio-based plastics is greatly dependent on LCA methodological assumptions, leading to a wide range of results for cradle-to-gate impacts of bio-based plastics. For example, biogenic carbon accounting is inconsistent across studies, with some treating it as "carbon neutral" while others assign it values similar to fossil carbon. Similarly, impacts associated with upstream agricultural processes for bio-based materials are sometimes allocated based on the market value (economic allocation), which can be close to zero for 2nd generation feedstocks, and therefore severely underestimate the environmental impacts of the production process of these feedstocks. This variability underscores the need for reporting standards specific to life cycle assessments of bio-based materials. Standardization would facilitate consistent comparisons of different bio-based

production routes for plastics, expedite research progress, and offer clearer data for policymakers and industry stakeholders.

2.2 End-of-life impacts

Given the lack of robust experimental studies that examine the biodegradation behavior of bio-based plastics in landfills, further research should investigate the sensitivity of the biodegradation behavior of these materials to environmental factors. This is especially relevant given that 72% of all plastics ever made have ended up in landfills [10]. Additionally, despite the prevalence of biodegradation studies of bio-based plastics in composters and anaerobic digesters (ADs), many of these studies have been conducted on a lab scale which allow for greater control over environmental conditions than commercial scale composters and anaerobic digesters. Further, many of the experimental studies were based on AD standards which require complete biodegradation within 2 months, despite many commercial ADs operating on much shorter timescales. Therefore, future work should investigate methods, such as pretreatment options, that can help accelerate the biodegradation behavior of these materials, and work could be expanded to better understand the impact of non-biodegraded plastics on compost quality.

Improved metrics are needed to assess EoL resources and their utilization. In this study, a cut-off approach is used for recycled plastic and therefore no credits are applied for the avoidance of virgin plastic production. However, there is no standard for how to apply credits at EoL stages of materials. For example, given the uncertainty around the quality of recycled plastics, there are inconsistent assumptions in the literature regarding the substitution ability of these materials, leading to high variability among LCA results. Further research should develop consistent

methods for capturing product circularity within LCAs, allowing for more reliable comparisons of end-of-life options for plastics. Similarly, further research is needed to investigate the recyclability of biodegradable bio-based plastics such as PLA, PHB and TPS, and the impacts of mixed plastic waste streams (biodegradable and non-biodegradable materials) on the quality of recycled plastic.

Plastics separation and recycling pathways require further study. A major challenge in managing end-of-life treatment for plastics is the prevalence of mixed plastic waste streams, which complicates sorting and recycling processes. Therefore, developing recyclable-by-design plastics, or mono-material plastic packaging is essential for enhancing recycling efficiency.

Another major challenge for end-of-life treatment of bio-based plastics specifically is the lack of standardized labeling and inadequate access to effective waste management infrastructure.

Therefore, future research should focus on the impact of implementing clear and consistent labeling for bio-based plastics, aiding consumers in identifying and properly sorting their plastic waste. Finally, common bottlenecks for plastic recycling, include high costs and inefficiencies in collection and sorting processes. Future research should aim to improve the efficiency of sorting processes at material recovery facilities (MRF) to help reduce the amount of plastics sent to incinerators and landfills. Exploring advanced recycling methods, such as chemical recycling, is critical for enhancing the circularity of plastics, particularly for hard-to-recycle plastics such as PVC. Most existing research has been limited to lab-scale studies and has shown that these processes can be highly energy-intensive. Therefore, further investigation of process improvements to increase the efficiency of chemical recycling processes is crucial to enable the scaling up of this waste treatment option.

2.3 Scaling up CDR potential

When implementing large-scale transitions to bio-based materials, assessing potential shifts in environmental burdens is essential. Future research should investigate the large-scale impacts of bio-based materials outside of GHG emissions and investigate solutions to avoid burden shifting. For example, given the various uses and growing demands for biomass (e.g. food, feed, energy, resources for the built environment, and consumer products), systematic assessments of the impacts on land-use changes and resource availability are necessary. Indirect land-use change impacts, often excluded from bio-based material LCAs, can result in significant GHG emissions and negatively impact ecosystems. As demand for bio-based materials increases, the conversion of carbon-rich ecosystems like forests, wetlands, and grasslands to cropland could significantly decrease soil organic carbon (SOC). Therefore, future research should focus on modeling efforts that could help investigate this shift in land use change and how changes in SOC might affect ecosystems. Further, investigation of biomass resources with limited to no land footprints, such as food waste, algae, and biogas, may become vital for scaling up bio-based products to meet consumer demand.

Despite being around since the early 1900's, bio-based plastics still only make up 1% of the plastic market. This low market share highlights the need for comprehensive future research to explore the economic viability of bio-based plastics and the potential for creating a more sustainable and cost-competitive bio-based economy. Detailed techno-economic assessments should evaluate the costs of scaling up production facilities, considering capital and operational expenses and the integration of advanced technologies for improved efficiency and productivity. Further research is needed to investigate potential economic incentives such as subsidies or tax

incentives, that could accelerate the expansion of a bio-based economy. Finally, developing efficient supply chains for bio-based materials, particularly from non-edible biomass resources, will be essential for investigating the logistics of sourcing, processing, and transporting these materials in a cost-effective and sustainable manner.

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Appendix A. Cradle-to-gate impacts of bio-based plastics

Supplementary Data S0-S20 (separate file, see DOI link in Chapter 2)

Data S0. Summary table ofecoinvent datasets, their process identifiers, and any modifications

Data S1. LCI for global average electricity grid production

Data S2. LCI for sugarcane production processing

Data S3. LCI for corn/corn stover production

Data S4. LCI for wheat/wheat straw production

Data S5. LCI for rapeseed production

Data S6. LCI for methane production from landfill biogas

Data S7. LCI for PLA production from corn, corn stover, and bagasse

Data S8. LCI for PHB production from sugarcane sugar and biogas

Data S9. LCI for TPS production from corn and reclaimed potato starch

Data S10. LCI for Bio-ethanol production from corn stover, wheat straw, and sugarcane molasses

Data S11. LCI for Bio-HDPE from corn stover, corn, wheat straw, and sugarcane molasses

Data S12. LCI for Bio-PET from corn and corn stover

Data S13. LCI for Bio-PTT from corn and corn stover

Data S14. LCI for Bio-PUR production from rapeseed oil

Data S15. LCI for Bio-PP production from used cooking oil

Data S16. Global crop yield calculations

Data S17. Source data for Figure 2.2

Data S18. Source data for Figure 2.3

Data S19. Data for supplemental figure 1

Data S20. References

Appendix B. End-of-life impacts of bio-based plastics

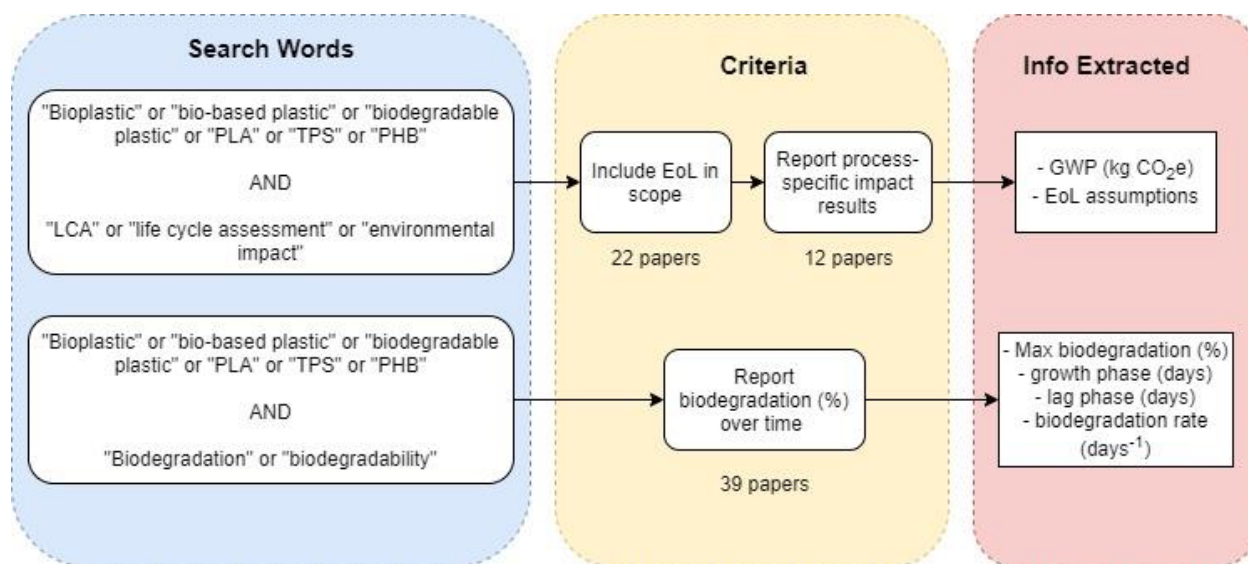


Figure S1. Literature review methodology flow chart

Table S1. Summary of material properties of common biodegradable bioplastics

Material	Chemical Formula	Density (g/cm ³) ^a	Carbon content (%) ^b	T _g (°C) ^c	HHV (MJ/kg) ^d
polyhydroxyalkanoates (PHAs)	(C ₉ H ₁₈ O ₆) _n	0.98 – 1.26	56%	-8 – 4	22.5
Poly-lactic acid (PLA)	(C ₃ H ₄ O ₂) _n	1.2 – 1.36	50%	45 – 60	18.6
Thermoplastic starch (TPS)	(C ₆ H ₁₀ O ₅) _n	1.3	44%	18 – 132	15.16

^a values from [427–429]

^b approximate values based on stoichiometry, not accounting for parameters such as additives, inclusions, grafting

^c values from [174,427,430,431]

^d values from [432–434]

Table S2. Overview of LCA papers of bioplastics that include end-of-life in scope (where ‘MR’ indicates mechanical recycling and ‘AD’ indicates anaerobic digestion)

Reference #	Materials studied	# of impact categories	End-of-life options examined
[435]	PLA, Mater-Bi	11	MR, compost
[269]	PLA, Mater-Bi	3	incineration, MR, compost, AD
[436]	PLA, PHAs, PBS, PP	18	Landfill, compost, MR, incineration
[164]	PLA, TPS	1	Landfill, compost, MR, incineration, direct fuel substitution, AD
[437]	PLA, PET, aluminum, glass	1	Landfill, MSWI, recycle
[282]	PLA, TPS, PET, Bio-PET, HDPE, Bio-HDPE, LDPE, Bio-LDPE, PET, HDPE, LDPE	10	MR, compost, landfill
[438]	Bio-HDPE, HDPE	11	incineration, MR
[439]	PHB	5	Compost, landfill
[153]	Bio-LDPE, LDPE	5	Incineration, landfill
[440]	PET, Bio-PET, Recycled PET, Recycled Bio-PET, PLA	2	Incineration
[441]	ABS, PC/PLA, PA1010	1	incineration
[280]	PLA, PHA, Mater-Bi	2	incineration, AD, compost
[442]	PLA, PCL, PP	4	incineration, landfill, compost
[443]	PLA, PS	10	incineration
[444]	PLA, LDPE, HDPE	7	incineration, landfill, compost
[445]	PLA, PET, PS	9	incineration, landfill, recycle
[446]	PLA, PS	9	incineration, compost
[271]	PLA, PET	11	incineration, landfill, MR, compost
[447]	PHA, PP	4	incineration, landfill, compost
[448]	PLA, LDPE	1	Incineration, landfill, recycle
[147]	PLA	3	MR, chemical recycling, compost
[281]	PLA	5	incineration, compost, landfill, chemical recycling

Table S3. Overview of biodegradation studies of PLA where ‘meso’ indicates mesophilic and ‘thermo’ indicates thermophilic.

Ref #	compost max biodeg (%)	AD temp	AD max biodeg (%)	landfill max biodeg (%)	Testing method	sample size/type
[222]	86				CO2 evolution	2 x2 cm plate, 0.3 mm thick
[247]		meso	0		Biogas evolution	1.6 cm plate, 1.2 mm thick
[224]	96				CO2 evolution	0.45 mm thick strips
[223]	70				CO2 evolution	5x5 cm, 0.035 mm thick
[215]	90	meso, thermo	0,58		CO2 evolution, biogas evolution	0.5x10 cm, 0.03 mm thick
[245]		meso	26		Biogas evolution	powder, 125-250 um
[243]		thermo	70		Biogas evolution	powder, 125-250 um
[225]	100				CO2 evolution	powder
[217]				0	Biogas evolution	20x40 mm, 0.05-0.075 mm thick
[216]				37	Biogas evolution	pellets
[242]		thermo	80,85		Biogas evolution	powder, 0.025 mm thick films
[246]		thermo	89		Biogas evolution	powder, 125-250 um
[240]		meso, thermo	0,100		Biochemical methane potential	drinking cup
[244]		thermo	93		Biogas evolution	powder, 125-250 um
[241]		meso	0		Biochemical methane potential	0.15 mm particles

Table S4. Overview of biodegradation studies of PHB

Ref #	Type of PHA	compost max biodeg (%)	AD temp	AD max biodeg (%)	landfill max biodeg (%)	Testing method	sample size/type
[249]	PHBV		meso	86		Biogas evolution	0.01-3.9 mm
[250]	PHBO		meso	88	45	Biogas evolution	
[247]	PHB		meso	69 - 100		Biogas evolution, mass loss	0.24mm and 5 mm thick plates
[233]	PHB	45 - 100				Mass loss	0.24mm and 5 mm thick plates
[251]	PHB, PHBV		meso	29 - 100		Biogas evolution	thin film (100 um)
[223]	PHB	75				CO ₂ evolution	5x5 cm, 0.035 mm thick
[245]	PHB		meso	90		Biogas evolution	powder, 125-250 um
[243]	PHB		thermo	98		Biogas evolution	powder, 125-250 um
[234]	PHBV	63				CO ₂ evolution	
[225]	PHBV	95				CO ₂ evolution	powder
[235]	PHB, PHBV	80 - 90				CO ₂ evolution	thin film (90 um, 80 um)
[236]	PHBV	80				CO ₂ evolution	thin film
[252]	PHB, PHBV		meso	83 - 96		Biogas evolution	
[253]	PHBV		meso	90		Biogas evolution	powder
[217]	PHBV				85	Mass loss	0.05-0.075 mm thick film
[239]	PHBV	100	thermo	91		Biogas evolution	film

[237]	PHB	50				Mass loss	
[238]	PHB	92				CO2 evolution	pellets
[241]	PHB		meso	80-98		Biochemical methane production	0.15 mm particles
[219]	PHB	70	meso	80		CO2 evolution, Biogas evolution	powder (200 um)

Table S5. Overview of biodegradation studies of TPS

Ref #	Type of TPS	compost max biodeg (%)	AD temp	AD max biodeg (%)	landfill max biodeg (%)	Testing method	sample size/type
[227]	corn starch and 25 wt% glycerol	73				CO2 evolution	powder
[228]	wheat starch, glycerol, water	57				CO2 evolution	1-2 mm powder
[219]	Mater-Bi AI05H, Mater-Bi ZF03U	22 - 60	meso	22		CO2 evolution, biogas evolution	.035 mm film
[229]	Mater-Bi ZI01U	100				Mass loss	35 x 15 x 1.5 mm
[230]	Mater-Bi ZI01U	72	meso	21-25		Mass loss	
[221]	65% (w/w) cassava starch, 35% (w/w) glycerol	73				Mass loss	
[248]	35.0 g potato starch, 15.0 g glycerol		meso	69		Biogas evolution	0.12 mm film
[231]	55% PCL, 30% starch, and 15% aliphatic polyesters	88		83		Oxygen consumption, Biochemical methane potential	

[220]	starch, glycerol (30 wt. %) and distilled water (water/starch = 6/1)	100					CO2 evolution	2 mm plates
[232]	MaterBi	43					Mass loss	15 x 15 cm
[226]	MaterBi	88					Mass loss	5x5, 50 µm thick

Table S6. GHGs (kg CO₂e/kg PLA) at end-of-life from LCAs

Ref EoL	[164]	[267]	[280]	[268]	[80]	[445]	[281]	[282]	[155]	[147]
recycle	-0.4 – 0.6	-1.9 – 0.5		-0.6 – 0.7		0.5				
incineration	1.9	1.1 – 1.9	1.2 – 1.8	1.3	1.8	2.3	-0.2			0.4
compost	1.8 – 1.9		2	1.7			0.1	0.3	1.6	3
AD	0.9 – 2.2									
landfill	0.1			0				0.1 – 2.7	0 – 1.8	

Table S7. GHGs (kg CO₂e/kg TPS) at end-of-life from LCAs

Ref # EoL	[164]	[280]	[282]
recycle	-0.6 - 0.6		
incineration	1 - 2	1 – 1.6	
compost	1.8 – 1.9	1.4	0.3
AD	0.9 – 2.1	0.6 – 1.3	
landfill	6.4		1.2

Table S8. GHGs (kg CO₂e/kg PHB) at end-of-life from LCAs

Ref # EoL	[280]	[268]	[449]	[254]
recycle		-1.6 – 0.8		
incineration	1.3 – 2.1	1.3		
compost	1.8	1.9	3	
AD	0.7 – 1.7			
landfill		3.4		-0.4 – 1.3

Appendix C. Global-scale Carbon dioxide removal (CDR) with bio-based plastics

S1. Cradle-to-gate plastic impacts. The cradle-to-gate impacts (namely the combined GWP of CO₂, CH₄ and N₂O emissions) for bio-based plastic production were derived from [297] using a mass-based allocation approach. When multiple feedstocks were presented, an average value was used. For example, Van Roijen and Miller [297] present results for bio-based PLA made from both corn stover and sugarcane bagasse. Therefore, in this study, the GHG emissions of both production routes are averaged together to obtain an estimate for the cradle-to-gate impacts of PLA from 2nd generation feedstocks. See supplemental dataset, Sheet 3, for a full list of these assumptions. The LCI for the 2018 global average electricity grid, as well as the renewable energy scenario (wind electricity, and biogas energy), come from [297]. The impacts for fossil-based plastic were derived from ecoinvent [73]. The only modification made to the petroleum-plastic inventories was the electricity grid, which was either set to the 2018 global average electricity grid or wind electricity depending on the scenario.

S.2 End-of-life plastic impacts. The GHG emissions associated with bio-based plastic disposal in landfills, incineration, composting, anaerobic digestion, and mechanical recycling come from [37]. The impacts of chemical recycling of mixed plastic waste via pyrolysis was calculated using the inventory reported in [301] and by applying CO₂, CH₄ and N₂O GWP factors reported in the sixth IPCC report [1]. The only modification made to the inventory was the electricity grid, which was either swapped out with the 2018 global average, or wind electricity depending on the scenario. A similar approach was utilized to calculate the impacts of alternative chemical

recycling methods (e.g. glycolysis, hydrolysis) reported in literature (See Supplemental Dataset, Sheet 7).

S.3 Identifying carbon dioxide removal (CDR) scenarios. The weighted average production and end-of-life emissions were combined to determine the total impacts per kg of plastic under various scenarios. Scenarios resulting in a GWP of less than -0.1 kg co2e/kg plastic were considered CDR scenarios and are reported in Supplemental Dataset, Sheet 8. Aside from the total emissions (which are reported in terms of kg CO2e/kg plastic), all other variables are reported as a decimal from 0 to 1, representing the fraction of implementation. For example, a chemical recycling value of 0.2 for biodegradable plastics signifies that 20% of biodegradable bio-based plastics are disposed of via chemical recycling (specifically pyrolysis). Similarly, a value of 0.9 for “bio-based plastic market”, means that 90% (by weight) of plastics are assumed to be made using bio-based resources. It is important to note that only 2nd/3rd generation feedstocks were considered as bio-based resources when examining CDR scenarios to avoid competition with food.

S.4 Resource availability. The global annual production of feedstocks was derived from FAO [72]. The availability of used cooking oil was determined by taking the total annual production of vegetable oil, and multiplying it by the expected yield of used cooking oil reported in literature [450]. The availability of biomethane was determined using global biomethane potential (reported in MJ) [451] and the energy density of biomethane [452]. Availability of wheat straw and corn stover were determined assuming that 30% and 2/3 of the residues are needed on the field as a soil amendment, as reported in [297]. Furthermore, the ratio of

byproduct yield to main crop for corn and wheat were assumed to be 1 and 1.3, respectively [297]. The annual production of sugarcane molasses was calculated assuming a 5% weight yield of molasses per kg of sugarcane production [297].

S.5 Roadmap to 2050. The global annual emissions for plastics were determined by combining the weighted-average production and end-of-life impacts per kg of plastic. The emissions associated with plastic production were calculated by taking a weighted average of the carbon footprints of plastics based on their projected market share. Similarly, a weighted average of end-of-life emissions were determined assuming the make-up of plastics at end-of-life is the same as the make-up of plastic production. It was assumed that the make-up of the plastic market will stay the same in the future (with the exception of bio-based plastic alternatives being substituted in). The market make-up of plastics was therefore determined using the 2022 market distribution of plastic [19] as a baseline, and then determining bio-based plastic market replacements based on their technical substitution potential as reported in supplemental data sheet 1 (SDS1). These emissions were then scaled globally by multiplying the calculated carbon intensity by the anticipated mass of plastic consumption in that year. To account for the impact of plastic recycling on annual plastic production, the total mass of recycled plastic is multiplied by a substitution factor of 0.9 or 1 for thermomechanical and chemical recycling respectively [41], and then subtracted from the total demand to determine the quantity of virgin plastic production. The annual consumption of plastics was determined assuming an annual growth in plastic demand of 4% per year. From there, the quantity of virgin plastic production was calculated by subtracting the quantity of plastics that were anticipated to be recycled in that year.

Supplementary Data S1-S18

Note: the full list of (over 100,000) CDR scenarios can be found in the attached supplemental material excel file.

Table S1. Substitution potential of bio-based plastics

% substitution of fossil-based plastic															
Bio-based plastic	LD PE	HDPE	PP	PVC	PS	PET	PUR	PA	ABS	PC	PBT	other polyacrylates	PMMA	epoxy resins	Syn. rubber
starch plastics (TPS)	8	8	8		8		8						4		
PLA		10	10		10	20		10					5		
PHA	20	20	10	10	20	10	10		10				5		
cellulose films*			10	10	10	15									
Bio-PE	72	62													
Bio-PP			57												
Bio-PVC				80											
Bio-PET						35									
Bio-PTT			5			20		30		20	100		5		
Bio-PUR							80								
Bio-PA*								30							
Bio-PB*															80
Bio-ABS*									90						
bio-polyacrylates*												100			
Bio-epoxy resins*														75	
total sub	100	100	100	100	48	100	98	70	100	20	100	100	19	75	80

*plastics not modelled in this study. A carbon footprint equal to the average of all other bio-based plastics is assumed.

References: [18]

Table S2. Current (2022) fossil-based plastic market

Plastic type	% of market
LDPE	16
HDPE	13
PP	21
PVC	14
PET	7
PUR	6
other	23

References: [19]

Table S3. Potential future plastic market (assuming 90% replacement of petro-plastic with bio-based plastic)

Plastic type	% of market*
PLA	5
PHB	11
TPS	5
Bio-PE	20
Bio-PVC	11
Bio-PUR	5
Bio-PP	12
Bio-PET	2
Bio-PTT	6
other bio-based	15
PUR	0
other (petro-based)	7

*The percent of market share is determined by combining the substitution potential (Table S1) of the plastic with the current plastic market (Table S2).

Table S4. Bio-based plastic end-of-life impacts

Plastic type	GWP (using 2018 average global electricity grid)	GWP (using 100% renewable energy)	Assumptions
PLA (1st gen)	1.3	-1.3	Corn feedstock
PLA (2nd gen)	1.7	-1.1	Average impacts of corn stover and sugarcane bagasse
PHB (1st gen)	0.9	-1.7	sugar from sugarcane feedstock
PHB (2nd gen)	1.6	-9.3	Impacts of PHB production from biogas. Assuming 50% of carbon credits are in the form of avoided CO ₂ , and 50% in the form of avoided CH ₄
TPS (1st gen)	1.4	0.019	Corn starch feedstock
TPS (2nd gen)	1.3	-0.043	reclaimed potato starch feedstock
Bio-PE (1st gen)	-1.1	-2.4	corn feedstock
Bio-PE (2nd gen)	1.4	-0.93	Average impacts of corn stover, wheat straw and sugarcane molasses
Bio-PVC (1st gen)*	0.098	-1	corn feedstock
Bio-PVC (2nd gen)*	1.3	-0.48	Average impacts of corn stover and sugarcane molasses feedstocks
Bio-PUR (1st gen)	2.4	0.77	rapeseed oil feedstock
Bio-PUR (2nd gen)	2.1	0.68	used cooking oil feedstock
Bio-PP (1st gen)	-1.7	-2.7	rapeseed oil feedstock
Bio-PP (2nd gen)	-2	-2.9	used cooking oil feedstock
Bio-PET (1st gen)	1.7	-1	corn feedstock
Bio-PET (2nd gen)	2.3	0.53	corn stover feedstock
Bio-PTT (1st gen)	1.9	-1.2	corn feedstock
Bio-PTT (2nd gen)	1.5	-0.13	assuming bio-PDO from corn, and bio-PTA from corn stover
other bio-based (1st gen)	0.77	-1.2	Average of all 1st generation bio-based plastics
other bio-based (2nd gen)	1.2	-1.5	Average of all 2nd generation bio-based plastics
PE	2	0.81	Based on ecoinvent inventory
PVC	2.23	0.517	Based on ecoinvent inventory
PUR*	4.825	2.87	Based on ecoinvent inventory
PP	1.77	1.09	Based on ecoinvent inventory
PET	3.04	0.915	Based on ecoinvent inventory
other petro-based	2.773	1.2424	average of above petro-based plastics

*Impacts of PUR reflect an average of rigid and flexible PUR foam

References: [297]

Table S5. End-of-life impacts (in kg CO₂e/kg plastic) of bio-based (and petro-based) plastics.

plastic type	landfill (w/o gas capture)	landfill (with gas capture)	incineration	compost	AD (meso)	AD (thermo)	Mech. recycling	Mech. recycling (renewable energy)	pyrolysis chemical recycling **	pyrolysis chemical recycling (renewable energy) **
	2.9									
PLA	1	0.62	1.8	1.4	0.06	1.73	0.41	0.007	1.62	0.03
	9.0									
PHA	3	1.79	2	1.64	2.15	2.15	0.41	0.007	1.62	0.03
	0.7									
TPS	3	0.16	1.63	0.42	0.15	0.30	0.41	0.007	1.62	0.03
PE/ Bio-PE	0	0	3.1	0	0	0	0.41	0.007	1.62	0.03
PVC/ Bio-PVC	0	0	1.4	0	0	0	0.41	0.007	1.62	0.03
PUR/Bio-PUR	0	0	2.37	0	0	0	0.41	0.007	1.62	0.03
PP/Bio-PP	0	0	3.14	0	0	0	0.41	0.007	1.62	0.03
PET/Bio-PET	0	0	2.3	0	0	0	0.41	0.007	1.62	0.03
PTT/Bio-PTT	0	0	2.35	0	0	0	0.41	0.007	1.62	0.03
other (bio/petro)*	0	0	2.23	0	0	0	0.41	0.007	1.62	0.03

*Calculated by taking the average end-of-life impacts of non-biodegradable bio-based plastic materials

** chemical recycling impacts were derived from literature

Note: non-biodegradable bio-based plastics have the same end-of-life emissions as their fossil-based counterparts

References: [37,301]

Table S6. Resource availability assessment for bio-based plastics modelled herein

Bio-based plastic	feedstocks	kg feedstock required/ kg plastic	Plastic demand (Mt)	Resource avail. Mt (2022)	% of resources consumed to meet current demand	% of resources consumed to meet 2030 demand	% of resources consumed to meet 2040 demand	% of resources consumed to meet 2050 demand
PLA	corn	1.5	21.3	1163.0	2.7	2.7	2.9	2.8
	corn stover	2.7	21.3	814.1 ^a	7.0	14.8	15.8	15.1
Bio-PE	sugarcane molasses ^e	5.1	76.3	96.1	405.2	405.0	431.7	412.9
	wheat straw ^f	3.8	76.3	350.1	82.9	82.8	88.3	84.4
	corn stover	4.0	76.3	814.1 ^a	37.5	37.5	40.0	38.2
TPS	34% bio-based from corn starch	0.3	18.6	1163.0	0.5	0.5	0.6	0.5
	34% bio-based from reclaimed potato starch used	0.3	18.6	74.942 ^c	8.3	8.3	8.9	8.5
Bio-PP ⁱ	cooking oil ^b	236.4	46.4	64.3	17057.4	17048.7	18174.4	17383.7
	rapeseed oil ^g	236.4	46.4	26.6	41245.6	41224.4	43946.6	42034.5
Bio-PVC	corn stover	1.9	43.8	814.1 ^a	10.2	10.2	10.9	10.4
	wheat straw ^f	1.8	43.8	350.1	22.5	22.5	24.0	22.9
Bio-PUR ^h	rapeseed oil ^g	0.4	18.3	26.6	27.5	27.5	29.3	28.0
	used cooking oil ^b	0.4	18.3	64.3	11.4	11.4	12.1	11.6
PHB	sugarcane sugar	1.8	44.8	192.0	42.0	42.0	44.7	42.8
	biomethane	5.3	44.8	595.8 ^d	39.5	39.3	41.9	40.1
Bio-PET	corn	3.9	9.4	1163.0	3.1	25.6	27.3	26.1
	corn stover	7.0	9.4	814.1 ^a	8.0	65.6	69.9	66.9
Bio-PTT	corn	4.2	25.0	1163.0	9.0	9.0	9.6	9.2
	corn stover	7.6	25.0	814.1 ^a	23.3	23.3	24.8	23.7

^a assuming 1:1 ratio of corn to corn stover and 30% of stover is left on the field as soil amendment

^b resource availability was determined using total vegetable oil production in 2021, and assuming 0.32 kg of used cooking oil is produced per kg of vegetable oil

^c Assuming 100% recovery of potato starch and 0.202 kg potato starch/kg potato

^d Assuming 32 EJ of biomethane produced annually, and biomethane has an energy density of 36 MJ/m³

^e Availability of feedstock was calculated assuming molasses yield is 5 wt% of total sugarcane production

^f Availability of feedstock was determined assuming a yield of 1.3 kg wheat straw/kg wheat, and that 2/3 of wheat straw is left on the field as a soil amendment

^g Rapeseed production is from 2021 FAO data

^h Feedstock requirements are calculated using an average of inputs for flexible and rigid PUR foam.

Inputs required for polyol production are assumed to be the same for used cooking oil and rapeseed oil

ⁱ Input requirements for bio-based naphtha production are assumed to be the same for used cooking oil and rapeseed oil

references: [72,450–452]

Table S7. Current and future plastic demand (accounting for increases in recycling rates)

Year	Virgin plastic production (Mt)	% Recycled content
current	390	9
2030	389.8	27
2040	415.54	47
2050	397.46	66

Table S8. US Department of Agriculture TRL criteria

Activity	TRL scale	Description
Preliminary Technology Solution Evaluation	1	Challenge/opportunity identified
Preliminary Technology Solution Evaluation	2	Solution or approach formulated.
Experimental Testing	3	Proof of concept experiments
Experimental Testing	4	Field trials or validation experiments
PreCommercial Assessment	5	Validate commercial acceptance (conduct field-scale production trials to determine production costs, market potential, or other limitations)
PreCommercial Assessment	6	Full-scale production initiated. Ensure materials can be sourced for full-scale production
Commercial Deployment	7	Market availability. Commercial-scale production by producers or manufacturers occurs with delivery of products to producers, handlers, processors, distributors, or other supply chain participants to market outlets and for meeting user demand.
Commercial Deployment	8	Commercial use established. On-going system-level monitoring and research to improve the production system or technology application while managing multiple natural and human resources concerns across entire supply chains.
Commercial Deployment	9	Sustained production capacity. A full array of private and public sector services are available to support system-level production, handling, distribution, and markets across entire supply chains.

References: [346]

Table S9. TRL levels for bio-based plastics and their respective justifications

Bio-based plastic	Feedstock type	TRL	Justification of TRL level	Relevant companies
PLA	1st gen (corn, sugarcane)	9	Full scale production reached. Would require 3% of available corn to meet current demand.	NatureWorks, TotalEnergies Corbion, futerro
	2nd gen (lignocellulosic crops)	3	Current production is in experimental phase	n/a
TPS	1st gen (corn)	9	Full scale production reached. Would require 1% of available corn to meet current demand.	Novamont, Kuraray, Biotec
	2nd gen (lignocellulosic crops or waste starch)	3	Current production is in experimental phase	n/a
Bio-PE	1st gen (sugarcane molasses)	7	Full scale production reached but global supply of sugarcane molasses is not sufficient to meet demand. 256% of currently available molasses would be required.	Braskem
	2nd gen (lignocellulosic feedstocks)	9	Full scale production reached, does not compete with food, requires 23% of currently globally available corn stover.	Borealis
Bio-PVC	2nd gen (lignocellulosic crops)	9	Full scale production using lignocellulosic feedstocks. Would require 10% of currently globally available corn stover/wheat straw.	Ineos
PHB	1st gen (sugarcane sugar)	7	Full scale production reached but would require 45% of currently available sugar to meet demand which would put a strain on food resources.	PHB industrial
	2nd gen (biomethane)	6	Companies are in the process of validating full scale production.	Mango Materials
Bio-PP	2nd gen (waste vegetable oil)	6	Full scale production reached, but global supply of waste vegetable oil is not sufficient to meet demand (would require a 200-fold increase in available resources).	Borealis
Bio-PUR	1st gen (vegetable oil)	7	Full scale production of bio-based polyols reached, but would require 31% of available rapeseed oil which competes with food resources.	PolyLabs
	2nd gen (waste vegetable oil)	3	Current production is in experimental phase	n/a
Bio-PET	1st gen (corn/sugarcane molasses)	5	Companies are conducting field-scale production 100% bio-based PET. Partially bio-based PET is on the market.	Coca-Cola, Suntory
	2nd gen (lignocellulosic crops)	3	Current production is in experimental phase	n/a
Bio-PTT	1st gen (corn)	5	Bio-based PDO (one of the main inputs), is being produced commercially, but bio-based terephthalic acid is still in prototype phase.	Covation Bio PDO

2nd gen	3	Current production is in experimental phase	n/a
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Table S10. Mixed plastic waste recycling via pyrolysis (values used in this study)

Output	Quantity	Unit
chemically recycled mixed plastic waste	1	kg
Inputs		
electricity	2.312	kWh
heat	0.326	MJ

References: [301]

Table S11. Alternative inventory for mixed plastic waste recycling via pyrolysis

Output	Quantity	Unit
chemically recycled mixed plastic waste (pyrolysis)	1	kg
Inputs		
diesel	0.049	kg
nitrogen, gas	0.11	kg
water	1	L
sand	0.0085	kg
heat	0.897	MJ
electricity	0.38	kwh
Emissions to air		
CO ₂	0.445	kg
NO	0.0057	kg
sulfur dioxide	0.0011	kg
carbon monoxide	0.000756	kg
methane, fossil	0.01165	kg
particulate	0.00342	kg
volatile organic compounds	0.000658	kg

References: [360]

Table S12. LCI for PET recycling via hydrogenolysis

chemically recycled PET	1	kg
Inputs		
PET	1	kg
dioxane	1	kg
ruthenium	0.008	kg
triflimide	0.002	kg
natural gas	2.8	m3
electricity	0.15	kwh
Emissions		
benzene dimethanol	1.2	kg
ethylene glycol	0.2	kg
ruthenium	0.008	kg
dioxane	0.48	kg

References: [361]

Table S13. LCI for PET recycling via hydrolysis

Output	quantity	unit
chemically recycled PET	1	kg
Inputs		
PET	1	kg
sulfuric acid	3.4	kg
sodium hydroxide	1.42	kg
ethanol	12.1	kg
anionic, detergent	0.1	kg
water	9.3	
natural gas	0.65	m3
electricity	4.36	kwh
Emissions		
ethylene glycol	0.313	
sodium sulfate waste	4.8	
waste water	9.3	
terephthalic acid	0.843	
ethanol	12.1	
anionic detergent	0.1	

References: [361]

Table S14. LCI for PET recycling via glycolysis

output	quantity	unit
chemically recycled PET	1	kg
inputs		
PET	1	kg
manganese acetate	0.05	kg
propylene glycol, liquid	0.7	kg
water deionized	1	kg
natural gas	4.74	m3
electricity	4.32	kwh
emissions/waste		
polyester resin	1	kg
manganese oxide	0.05	kg
waste water	1	kg
dioxane	0.48	kg

References: [361]

Table S15. Summary of CO₂e for different chemical recycling routes

Type	GWP (kg CO ₂ e/kg of plastic waste) using non-renewable energy	GWP (kg CO ₂ e/kg plastic waste) using renewable energy
glycolysis (PG)	18.90	4.89
hydrogenolysis	11.32	4.69
pyrolysis	1.31	0.98
hydrolysis	6.62	2.09

Table S16. Source data for Figure 10 and associated assumptions

year	Emissions (MMT CO ₂ e) from plastics per year	Total plastic production (incl. recycled plastics) Mt	Virgin plastic prod. (Mt)	Bio-based plastic market (%)	Types of plastic substituted with bio-based alternatives	Incin. (%)	Land fill (%)	Com post /AD (%)	Mech recyc (%)	Chem. recyc (%)
2024	1080	390	358	1	n/a	19	72	0	9	0
2030 ^a	484	533	403	41	PLA, TPS, Bio-PVC, Bio-PE	20	52	2	27	0
2040	-110.5	790	453	78	PLA, TPS, Bio-PVC, Bio-PE, PHB, Bio-PUR, Bio-PET, Bio-PTT	15	19	19	47	0
2050	-261	1169	446	92	PLA, TPS, Bio-PVC, Bio-PE, PHB, Bio-PP, Bio-PUR, Bio-PET, Bio-PTT, "other" bioplastics	0	10	19	43	23

^a Assuming 100% renewable energy for electricity and heat requirements starting in 2030.

Table S17. Make-up of 2018 global average electricity grid

energy type	percent of grid
geothermal	0.3
natural gas	23.0
hard coal	38.0
municipal waste incineration	0.4
wind power	4.8
photovoltaic	2.1
biomass	1.9
nuclear	10.1
oil	2.9
hydropower	16.2

References: [297]

Table S18. Make-up of 2018 global average electricity grid

Study	Production in 2050 (MMT)	Business as usual GHG emissions (Gt)	Carbon optimal pathway GHG emissions (Gt)	Carbon intensity of plastic under optimal pathways (kg CO ₂ e/kg plastic)	Business as usual carbon footprint of plastic (kg CO ₂ e/kg plastic)
Stegmann et al.	1137	4.4	1	0.88	3.87
<i>This study</i>	1169	3	-0.016	-0.01	2.57
Meys et al.	1418	4.7	-0.03	-0.02	3.31
Zheng and Suh	1606	6.5	0.5	0.31	4.05

References: [9,41,42]

Appendix D. Applying a framework for achieving CDR in building materials

S.1. Material mass consumed annually

To determine the carbon dioxide removal (CDR) possible in building materials, first the mass of materials demanded annually were quantified (Supplementary data sheet 1):

- While there are many wood and wood-related products or outputs (including energy from wood resources) manufactured annually, here we only consider sawn wood and wood-based panels as wood products that would enter infrastructure systems. Based on data from the United Nations Food and Agricultural Organization, in 2016, these two wood categories amounted to approximately 824 million m³ of material [453]. While the densities of woods can vary, here we take a representative density of 1.5 g/cm³ [388] to determine a mass of wood to infrastructure applications as 1.24 Gt.
- The United States Geological Survey [454] reported that 4.15 Gt of cement was produced globally in 2016.
- Aggregate demand is not well tracked [425,455]. However, using cement production, it can be estimated that there is approximately 30 Gt of concrete production per year [25,454–456]. While there are several constituents that are used in the production of concrete, the most prevalent are hydraulic cement, water, and aggregates. Water demand is typically lower than cement demand, but it can be as high as cement demand per volume of concrete [457]. Therefore, estimating the mass of cement production and a nearly equivalent water demand, we can determine a proxy for aggregates in concrete as being the remainder of the concrete. As such, we use these values to approximate

aggregate production for use in infrastructure materials, such as concrete, as being approximately 21.7 Gt.

- Reported statistics indicate 335 Mt of plastics were produced in 2016 with an estimated 66 Mt of plastics going to building and construction uses [458].
- It is estimated that roughly 1.2 trillion bricks are produced each year [392]; although, we note, data reporting for bricks is limited. Using this reported statistic and assuming that each brick weighs roughly 2 kg, global brick production is estimated here to be 2.4 Gt.
- Global asphalt production, amounting to 0.112 Gt was obtained from the United Nations Industrial Commodity 2016 Statistics [459]. Given that asphalt bitumen typically comprises 5 wt% of asphalt pavement [460], the global production of aggregate for asphalt pavement production (2.1 Gt) was calculated.

S.2. CO₂ emissions from materials production

To determine CO₂ emissions associated with individual materials studied herein, the fraction of these materials used in construction as reported by Hertwich [6] are used in most cases.

However, for the quantity of cement and lime used in construction, estimates are made based on data from the United States Geological Survey [461]; for the quantity of plastics used in construction, data are from [462].

The production of these materials results in CO₂ emissions throughout the supply chain, with the majority of emissions being a result of energy used in manufacturing and process-related emissions (i.e., those from chemical reaction processes or otherwise derived directly from the material resources). Similar to the scope of assessment considering bound carbon within the

materials, process-related emissions are associated with the materials themselves, so we focus on these emissions. Process-related emissions from cement production result from decarbonization of limestone, amounting to roughly 0.52 kg CO₂/kg [463]. Whereas process related emissions for aggregate production for concrete and asphalt pavement are assumed to be negligible, as the recovery of these aggregates should not lead to large flows of chemical-reaction derived emissions. The process-related emissions associated with plastic production vary significantly based on the type of polymer; however, it has been found that roughly 44% of cradle-to-gate impacts are attributed to emissions from petroleum refining [9]; using this value, an average value of roughly 1 kg CO₂/kg plastic was used in this work. Chemical-derived emissions for brick production were assumed to be zero [464]. Process related emissions for bitumen production (i.e., the asphalt binder) were assumed to be negligible given that it is a byproduct (rather than main product) of crude oil refining.

While cement has minimal carbon content, limestone (which does contain carbon) is regularly interground with cement or used as a mineral filler in concrete or mortar. The Global Cement and Concrete Association report the use limestone in cement blends at approximately 7% by weight in 216 [465]. Higher interground carbon-based minerals or carbon-based filler assumed to be up to 15% has been proposed by the Portland Cement Association and used commonly in European countries as well as elsewhere for limestone [466]. This difference between the potential use of an interground or filler carbon-based material suggest an additional 8% of such a resource. While the literature on the use of biochar in concrete remains nascent; here we will estimate the influence on CDR potential if the full 15% of this carbon-based resource were from biochar [467].

The utilization of biochar as a mineral filler itself is not critical; however, it provides a pathway for a high carbon uptake resource to be used in cement-based composites, potentially mitigating cement demand. In the production of biochar, biomass at its end-of-life is converted to biochar-based materials via pyrolysis [389]. Biochar can be formed from a variety of biomass resources, such as agricultural crop residues. The use of these biochar resources can lead to net-negative emissions composites by overcoming emissions associated with production [468]. Biochar carbon contents can vary based on crop, pyrolysis method, and other factors [469], but is approximated here as 30-85% based on a range of biomass resources reported by Lee et al. [470].

S.3. Sensitivity of uptake parameters

A sensitivity analysis was performed to examine the effects of variation in material carbon content and the effects of level of implementation of these carbon-sequestering materials on potential CDR at the global scale. To examine the sensitivity of each parameter individually, global CDR was calculated for a baseline scenario, in which all carbon contents and implementation levels were assumed to be the midpoint value of the minimum and maximum values (e.g., if the level of implementation can be anywhere from 0 to 100%, then 50% was chosen as the baseline). From here, several permutations were performed to examine the change in global CO₂ uptake, when one individual parameter is changed to its minimum or maximum value. For wood, given that our model considers potential increases in consumption, rather than having one variable be “level of implementation” ranging from 0 to 100%, instead the sensitivity analysis examines the impact of varying increases in wood consumption from 0 to 20%. The results from this sensitivity assessment can be found in supplemental data sheet 5. A similar

sensitivity analysis was done using heatmaps to examine the impact of CDR in each material on a per kg basis (see supplemental data sheet 5).

S.4. Resource availability assessment

A resource availability assessment was performed. Here, we focus on quantifying the resources required to fully implement these carbon-sequestering materials in construction applications and the quantity of resources currently available that can meet those demands. Noting that many strategies considered rely on utilization of readily available calcium or magnesium sources (e.g., those found in Earth's crust), the two main additional source groups of materials that were examined herein include (1) mineral wastes (to form carbonate-based aggregates and carbonatable cements) and (2) agricultural or woody residues as fillers or feedstocks for cement, bricks, plastic, and asphalt.

S.4.1. Availability of mineral wastes

Global annual production of mineral wastes, including red mud, blast furnace slag, steel slag, mine tailings, biomass ash, lignite ash, and hard coal ash, was obtained from the Renforth [471]. In addition, the percentage of Ca and Mg in each waste stream was obtained from the literature [471,472]. Therefore, the total CaCO_3 and MgCO_3 that could be produced from these sources was calculated by first multiplying the mass of the mineral waste by the percent Ca and Mg content, and then multiplying that by the molar mass ratio of MgCO_3/MgO and CaCO_3/CaO . To determine the annual production of crushed concrete (which can also act as a carbonate-based aggregate source), the global average lifetime of residential (85 years), non-residential (50 years), and civil engineering (65 years) buildings, along with the global average market share of

these concrete applications (30%, 32% and 37% respectively), was used to estimate the concrete stock reaching end-of-life in 2016 [473] as seen in equation S2.

$$\text{Quantity of crushed concrete} = \sum(P_{2016-t_{r,n,c}} * M_{r,n,c}) \quad \text{S2}$$

Where P is the mass of concrete produced globally in the year 2016, $t_{r,n,c}$ and $M_{r,n,c}$ are the lifetimes and market shares of the residential, non-residential and commercial buildings, respectively.

Annual production of cement kiln dust (CKD) was determined using the CKD generation rate reported by the EPA [474], along with the global annual production of cement reported by the global cement and concrete association (GCCA) [475], these values can be found in supplemental data sheet 6.

S.4.2. Availability of agricultural and woody residue

Global annual production of crops and woody biomass was obtained from FAOStat [72], and the ratio of main crop to by-product is obtained from Shah *et al.* [476], and other sources [477–479]. The moisture content and carbon content of the agricultural by-products was obtained from Phyliss 2 [480]. The resulting carbon content available in agricultural residues was determined using equation S3.

$$\sum P_x * R_{x/y} * (1 - m_y) * C_y \quad \text{S3}$$

Where P_x is the mass of crop x produced globally in a given year; $R_{x/y}$ is the ratio of main crop 'x' to by-product 'y'; m_y is the moisture content (%) of agricultural by-product 'y'; and C_y is the carbon content (in terms of dry weight %) of agricultural by-product 'y'. A similar approach was

done for woody biomass; however, given that production quantities are reported in terms of volume, to determine the mass of woody residues, an average density of 0.29 tonne/m³ was used, based on data from Phyliss 2 [480]. The data for agricultural crop residues and woody biomass can be found in supplemental data sheet 6. To determine the availability of biochar, a similar equation is used (S4), where the dry mass of the residue is multiplied by the biochar yield (%). Biochar yield (B_y) for each residue was calculated using a pyrolysis model [481], assuming a 600°C-pyrolysis temperature, and utilizing average cellulose/hemicellulose/lignin and ash contents from Phyliss 2 [480].

$$\sum P_x * R_{x/y} * (1 - m_y) * B_y \quad \text{S4}$$

The total resources required for global implementation of the carbon-sequestering materials examined herein was determined assuming a 1:1 replacement ratio of carbon (e.g., a bio-based plastic with a carbon content of 0.4 would require 0.4 kg of carbon from biomass). We note that, due to process inefficiencies, this conversion from feedstock to building materials might require higher levels of biomass/mineral resources. When assuming a 3:1 ratio of feedstock to product, we find that 100% replacement of plastics, brick, and asphalt binder in construction with bio-based counterparts would only require roughly 15% of global annual biomass residue production. However, we note that 72% of total biomass residues would need to be pyrolyzed to generate enough biochar for 15 wt% replacement of cement under this scenario. The results of this additional sensitivity analysis as well as the calculations for the resource availability assessment can be found in supplemental data sheet 6.

S.5. Comparison of CDR removals to IPCC targets

In this study, total calculated CDR potential for the examined building materials is compared to the required CDR to reach 1.5°C and 2°C targets as reported in the IPCC sixth assessment report. For this analysis, we examine the minimum, median and maximum values as reported by the IPCC (see supplemental data sheet 7). To determine cumulative CDR by 2100, we assume a constant rate of material consumption (in line with quantities reported in supplemental data sheet 1) and assume full implementation of the CDR technologies examined herein. A range of results is presented based on the minimum and maximum carbon contents of each material and their associated CDR potential. See supplemental data sheet 7 for these results.

S.6. Goal and scope of carbon uptake calculator

The carbon uptake calculator allows users to identify the overall life cycle emissions of a material and gain insights into which life cycle stages contribute to or mitigate its potential to act as a carbon sink. A traditional GWP value is presented as well as a time-adjusted warming potential (TAWP) value. Traditional GWP characterization factors assume that all life cycle emissions occur simultaneously. However, production emissions and end-of-life emissions can occur on very different time scales for some products such as building materials, which have long use-phases. Therefore, it is important to consider the impact of the timing of emissions release and uptake on cumulative radiative forcing using TAWP.

This calculator captures the impacts from the raw material acquisition to final disposal. The raw material life cycle stage refers to any emissions associated with the cultivation or extraction of the raw materials necessary to create the material. The processing/conversion step refers to

emissions associated with converting the raw materials into intermediates. Manufacturing and assembly refer to emissions associated with fabricating the final product at the factory gate. Construction refers to emissions occurring at the building site. Use phase emissions may include fluxes resulting from reactions occurring between the product and the atmosphere (e.g. carbonation of concrete during useful life results in CO₂ uptake), or from maintenance. Removal/demolition refers to any emissions resulting from deconstruction, such as emissions from operating machinery. End-of-life emissions include fluxes associated with waste treatment such as CO₂ emissions from incineration and recycling, CH₄ emissions from landfilling/dumping, or CO₂ uptake from carbonation (for end-of-life concrete).

S.7 TAWP calculation for carbon uptake tool

The impacts due to radiative forcing of a specific GHG are dependent on the year at which the flux (i.e., emissions or uptake) occurs and the magnitude of that flux, as seen in Equations 1 and 2 below. We assess net emissions associated with a product as a function of the inventory of fluxes and the TAWP to capture the radiative forcing from those fluxes as follows:

$$Net\ GHG\ emissions = \sum(Q_{i\ R,P,M,C,U,D,E,T} \times TAWP_{i\ R,P,M,C,U,D,E,T}) \quad Eq\ 1.$$

where $Q_{i\ R,P,M,C,U,D,E,T}$ is the quantity of GHG emissions or uptake associated with raw materials (R), processing (P), manufacturing (M), construction (C), use (U), demolition (D), end-of-life (E), and transportation throughout (T), respectively, and i is the type of GHG emission (here focusing on CO₂, CH₄ and N₂O).

To determine an appropriate TAWP, cumulative radiative forcing is addressed by calculating the integral of radiative forcing over a given time horizon. To capture the timing of emissions, an

additional variable "y" is incorporated to this equation, which is representative of the year that the emissions occurred. By subtracting "y" from the time horizon, the actual time horizon of the emission and its impact on cumulative radiative forcing are more accurately captured.

$$TAWP_{i R,P,M,C,U,D,E} = \frac{\int_0^{AT-y} RF_i}{\int_0^{AT-y} RF_{CO_2}} \quad \text{Eq 2.}$$

In Equation 2, RF_i and RF_{CO_2} refer to the radiative forcing of GHG i and CO_2 , respectively. AT refers to the analytical time horizon.

Similarly, to allow for comparisons with conventional GWP characterization factors, Equation 1 is also implemented with the Intergovernmental Panel on Climate Change's AR5 GWP 100a factors [482]. In this permutation, the GWP characterization factors for each GHG are used to replace the TAWP factors.

S.8 How to use the excel-based carbon uptake tool

To utilize the carbon uptake tool (provided in the attached supplementary excel sheet), make sure that macros are enabled in your excel sheet. Further, depending on the default security settings, the file may have to be “unblocked” upon downloading to allow for the enabling of macros.

S.8.1. Inputs

The carbon uptake calculator requires three types of inputs: (1) emissions (2) uptake and (3) life cycle stage duration. Start by clicking the ‘Clear inputs’ button to get rid of all the existing inputs in the tool. For each life cycle stage insert CO_2 , CH_4 and N_2O emissions in the “emissions” row and CO_2 , CH_4 and N_2O uptake in the “uptake” row. Note that values for uptake should be

inputted as a positive number. If there are no applicable emissions/uptakes occurring, then leave the cell value as zero. Be sure that all emissions and uptake are reported in terms of a consistent function unit (e.g. 1 kg or 1 m³ of material). Report the time period (in years) for each lifecycle stage. Note that the lifecycle stages with greyed out cells are assumed to be less than one year and therefore cannot be altered. Namely, (1) transportation from raw materials to processing/conversion, (2) processing and conversion, (3) transportation from processing/conversion to manufacturing and assembly, (4) manufacturing and assembly, (5) transportation from manufacturing /assembly to construction, and (6) construction, are all assumed to occur in one year. Similarly, (1) removal/demolition and (2) transportation from demolition site to end-of-life, are assumed to occur within one year. For the remaining lifecycle stages: raw materials, use/maintenance, and end-of-life, if the life cycle stage is longer than one year, be sure to report the total emissions/uptake occurring during the lifecycle stage (rather than emissions occurring per year). Note that if total lifecycle years are greater than 100, then impacts will only be captured for emissions occurring within the first 100 years.

After filling in all of the required inputs, click “Calculate Impacts” to see results. If additional permutations are desired, individual inputs can be edited or the “Clear inputs” button can be used to start over. Once the new inputs are entered, click “Calculate Impacts” again to see the new results.

S.8.2. Calculating outputs

With these inputs, the carbon uptake calculator determines the life-cycle global warming potential (from cradle-to-grave) for a specified unit of material using traditional global warming

potential (GWP) methods, as well as dynamic global warming potential (TAWP). Note that both traditional GWP and TAWP are calculated based on a 100-year time horizon.

The traditional GWP for each life cycle stage is determined by applying GWP100 factors for CO₂, CH₄ and N₂O of 1, 28 and 265 respectively, and by summing them together to determine the total CO₂e of that lifecycle stage.

To calculate the TAWP for lifecycle stages that are longer than 1 year, the emissions specified for that life cycle stage are assumed to be averaged out so that each year the same quantity of emissions occurs. From there, the TAWP is calculated using the equations 1 and 2 as specified in the methods.

The percent contribution of each life cycle stage is calculated by dividing the CO₂e of each lifecycle stage by the total CO₂e (both in terms of TAWP).

5.8.3. Interpreting results

All results are auto populated in the table on the right. Aside from the row labeled “TOTAL (GWP100)”, all results are reported in terms of the TAWP. The calculator provides the percent contributions of each life cycle stage to the overall TAWP, as well as the relative contribution of each GHG to help identify potential environmental impact hotspots and areas for process improvements. The columns labelled CO₂, CH₄ and N₂O, are showing the contribution (in terms of TAWP CO₂e) of CO₂, CH₄ and N₂O emissions and uptake occurring within each lifecycle stage, respectively. The column labelled “Total CO₂e”, represents the total CO₂e of each

lifecycle stage and is equal to the sum of the CO₂e of each GHG within that life cycle stage. Finally, the “process contribution” column reports the percent contribution of each lifecycle stage to the overall emissions of the product/process being examined. The overall TAWP (reported in cell N18), will be highlighted in green if the total is less than 0, and will be highlighted in red if it is greater than zero. Note that if the overall TAWP is negative, then the material is considered a carbon uptake material. In this scenario, any life cycle stages with positive percent contributions are attributing to carbon uptake, whereas life cycle stages with negative percent contributions are inhibiting carbon uptake.

Supplementary Data S1-S10, Figure S1

Supplementary excel-based carbon uptake tool is attached, and will be made publicly available upon publication of manuscript

Table S1. Global construction material consumption and process emissions

	Global production (Gt)	Global chemical emissions (Gt CO ₂)	Notes/assumptions
<i>Cement</i>	4.15	1.72	Chemical emissions for cement production include emissions from the decarbonation of limestone, which is assumed to be 0.52 kg CO ₂ /kg
<i>Concrete aggregate</i>	21.7	0	No chemical-related CO ₂ emissions are assumed to occur for aggregate production
<i>Plastic</i>	0.066	0.072	Given that chemical-emissions of plastics varies depending on the type of polymer, an average value of roughly 1 kg CO ₂ e/kg polymer is used
<i>Wood</i>	1.237	-2.27	Although CO ₂ is absorbed from and released to the atmosphere during wood cultivation and processing, it is not included herein because it is considered net-zero
<i>Brick</i>	2.4	0	No chemical-related CO ₂ emissions are assumed to occur for brick production
<i>Asphalt aggregate</i>	2.128	0	No process related CO ₂ emissions are assumed to occur for aggregate production
<i>Asphalt bitumen</i>	0.112	0	No process related CO ₂ emissions for asphalt bitumen production could be obtained and are therefore not included. It is also assumed that any emissions would be attributed to petroleum products and not to the bitumen by-product.
total	31.79	-0.48	

References:[9,25,460,463,464,72,388,392,454–456,458,459]

Table S2. Technical replacement ability of carbon-sequestering materials in construction

Carbon-sequestering material	Percent replacement of alternative technology	Assumptions
Carbonate-based aggregate	100%	Carbonate-based aggregates can have similar performance capabilities compared to traditional aggregate materials
Magnesium-oxide from magnesium silicate (MOMS) cement	85%	Long-term mechanical performance of alternative cements are still largely unknown, but maximum replacement levels are assumed here to highlight theoretical maximum uptake. Remaining 15% of mass is filler
Carbonatable calcium silicate cements (CCSC)	85%	same as above
Biochar cement filler	15%	Replacement levels above 15 wt% could contribute to changes in mechanical performance characteristics such as reduced compressive strength.
Bio-based plastics	100%	Bio-based, non-biodegradable plastics have identical properties to fossil-based plastics and therefore can replace nearly 100% of plastics used in construction
Bio-based asphalt bitumen	100%	fossil-based bitumen can be fully replaced with bio-oil due to their similar rheological and chemical properties
Biomass fiber-based brick	15%	Optimal compressive strength is achieved at biomass fiber replacement levels of 15 wt%
Portlandite brick	85%	Remaining 15% of mass is bio-based

note: wood is assumed to increase in production by 20%, but is not modelled as "replacing" any other materials

references:[381,386,395,397]

Table S3. Carbon dioxide removal (CDR) potential for carbon-sequestering materials

Carbon-sequestering material	minimum carbon uptake (kg CO ₂ /kg)	maximum carbon uptake (kg CO ₂ /kg)	notes/assumptions
Carbonate-based aggregate	0.44	0.52	Aggregate is either in the form of MgCO ₃ or CaCO ₃
Carbonatable cement (MOMS or CCSC)	0.22	0.52	
Biochar cement filler	1.10	3.12	Carbon content of biochar ranges from 0.3 to 0.85 kg C/kg
Bio-based plastic	1.47	3.30	Carbon content of plastic varies from 0.4 to 0.9 kg C/kg
Biomass fibers-based brick	0.22	2.20	Biomass fiber carbon content ranges from 0.4 to 0.6 kg C/kg
Portlandite brick	0.59	0.59	Brick is composed entirely of Ca(OH) ₂
Bio-based asphalt bitumen	1.1	2.57	Bio-based oil can have a carbon content of 0.3 to 0.7 kg C/kg
Wood	1.47	2.20	Carbon content of wood ranges from 0.4 to 0.6 kg C/kg

References: [384,385,396,399–401]

Table S4. Global CDR potential (minimum, average, and maximum values).

Carbon-sequestering material	minimum global CDR (Gt) *	average global CDR (Gt)**	maximum global CDR (Gt) ***
<i>Carbonate-based aggregate</i>	10.5	11.5	12.5
<i>Carbonatable-cement</i>	0.8	1.3	1.8
<i>Biochar cement filler</i>	0.7	1.3	1.9
<i>Bio-based plastic</i>	0.1	0.2	0.2
<i>Bio-based asphalt bitumen</i>	0.1	0.2	0.3
<i>Biomass fiber-based brick</i>	0.1	0.4	0.8
<i>Portlandite brick</i>	1.2	1.2	1.2
<i>Wood</i>	0.4	0.5	0.5
Total	13.8	16.6	19.3


* minimum uptake is assuming minimum carbon content, but keeping max replacement level the same

** avg uptake is assuming avg carbon content, but keeping max replacement level the same

*** max carbon uptake is assuming max carbon content, but keeping max replacement level the same

Table S5. Sensitivity of assumptions on total global CDR potential and per kg of material CDR potential

Min total global CO ₂ uptake (Gt)	Max total CO ₂ uptake (Gt)	Variable examined
8.37	8.43	Bioplastic carbon content
8.36	8.44	Bio-oil carbon content
8.35	8.45	wood carbon content
8.33	8.47	Brick biomass fiber carbon content
8.32	8.48	Bioplastic substitution %
8.30	8.50	Bio-oil asphalt substitution %
8.17	8.63	Change in wood consumption (%)
8.13	8.67	Carbonatable cement CO ₂ uptake
8.08	8.71	Biochar filler in cement carbon content
8.07	8.73	Biomass fiber-based brick substitution (%)
7.90	8.89	Carbonate-based aggregate CO ₂ uptake
7.89	8.91	Asphalt carbonate-aggregate substitution (%)
7.86	8.94	Biochar filler in cement substitution (%)
7.79	9.01	Portlandite brick implementation (%)
7.63	9.17	Carbonatable cement substitution (%)
3.17	13.58	Concrete carbonate-aggregate substitution (%)
median (baseline) value	8.40	



lowest to highest sensitivity

Figure S1. Sensitivity of assumptions on total CDR per kg of material

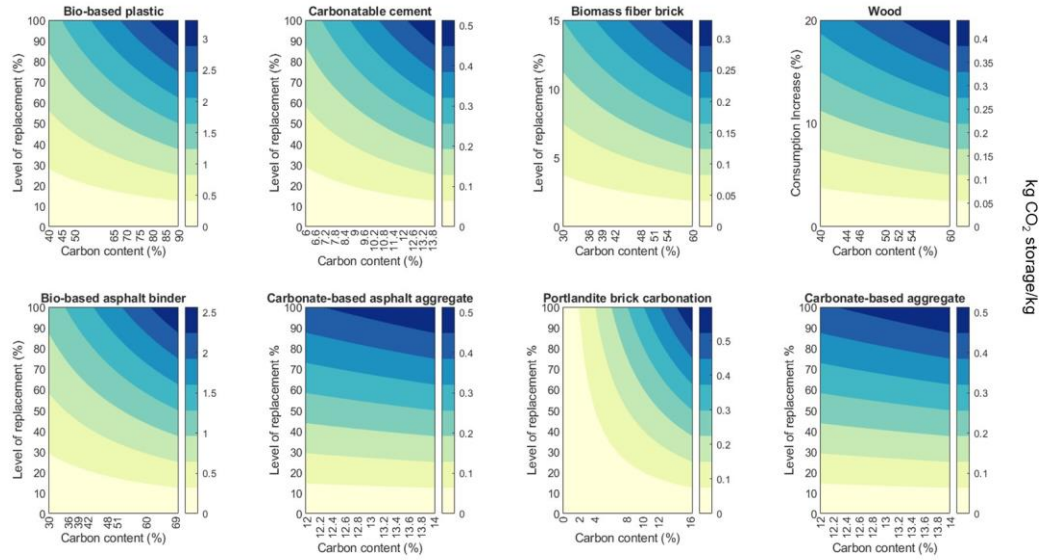


Table S6. Availability of mineral resources considered for carbonatable cement and aggregate

Source	Quantity (Mt/yr)	CaO (%)	MgO (%)	mass of CaCO ₃ (Mt)	mass of MgCO ₃ (Mt)
<i>crushed concrete*</i>	2147	0.14	0.0245	537	110
<i>red mud</i>	120	0.057	0.003	12	1
<i>blast furnace slag</i>	306	0.383	0.116	209	75
<i>steel slag</i>	194	0.371	0.091	129	37
<i>mine tailings</i>	50	0.021	0.238	2	25
<i>cement kiln dust</i>	840	0.44	0.016	660	28
<i>ash (biomass)</i>	200	0.298	0.07	106	29
<i>ash (lignite)</i>	60	0.202	0.058	22	7
<i>ash (hard coal)</i>	540	0.062	0.013	60	15

References: [471,472]

Table S7. Determining availability of crushed concrete as mineral resource

End-use categories (World)	Mean service life	Percent of world market	Year of production reaching EoL in 2020	global concrete produced in year of interest (Mt)	EoL concrete (Mt)
Residential	80	30%	1940	479.8	143.9
Non-residential	50	32%	1970	4348.7	1391.6
Civil engineering	65	37%	1955	1652.6	611.5

References:[473]

Table S8. Determining availability of cement kiln dust

global cement production	4200000000 tonnes
Cement kiln dust generation rate	0.2 tonnes/tonne cement

References: [474,475]

Table S9. Calculating annual production of agricultural byproducts and biochar

material	by-product to main crop ratio	% moisture content	% carbon (dry weight)	Annual global production of main-product in 2018 (Gt biomass)	Annual production of carbon source (Gt carbon)	Biochar Yield	Annual theoretical biochar production (Gt)
<i>barley straw</i>	1.47	0.12	0.41	0.14	0.09	0.35	0.0640
<i>maize stalk</i>	2.1	0.08	0.48	1.15	1.14	0.23	0.5075
<i>maize cob</i>	0.49	0.08	0.47	1.15	0.27	0.24	0.1254
<i>corn stover</i>	1	0.06	0.49	1.15	0.57	0.28	0.2983
<i>rice straw</i>	1.8	0.07	0.49	0.78	0.70	0.36	0.4728
<i>rice husk</i>	0.27	0.11	0.46	0.78	0.10	0.41	0.0772
<i>sugarcane bagasse</i>	0.4	0.22	0.50	1.91	0.38	0.25	0.1517
<i>wheat straw</i>	1.46	0.10	0.49	0.73	0.53	0.30	0.2952
<i>soybean straw</i>	2.81	0.06	0.43	0.34	0.42	0.28	0.2559
<i>sugarcane top/leaves</i>	0.18	0.08	0.50	1.91	0.17	0.40	0.1274
<i>rapeseed residue</i>	1.7	0.06	0.43	0.08	0.05	0.25	0.0305
<i>rye straw</i>	1.725	0.09	0.49	0.01	0.01	0.27	0.0045
<i>sorghum stalk</i>	1.99	0.06	0.45	0.06	0.05	0.23	0.0253
<i>almond hulls</i>	2.4	0.07	0.50	0.00	0.00	0.30	0.0022
<i>roundwood sawnwood residue</i>	0.42 (v/v)	0.20	0.54	1.15	0.26	0.25	0.0973
<i>sawnwood dust</i>	0.76 (v/v)	0.20	0.54	0.14	0.06	0.31	0.0268
<i>plywood residue</i>	0.24 (v/v)	0.20	0.54	0.14	0.02	0.31	0.0085
<i>plywood dust</i>	0.9 (v/v)	0.20	0.54	0.12	0.06	0.31	0.0263
<i>plywood dust</i>	0.1 (v/v)	0.20	0.54	0.41	0.01	0.31	0.0029
TOTAL annual carbon from agricultural residues and wood by-product production							4.87
TOTAL theoretical biochar production							2.60

Note: assuming wood density is 0.29 tonne/m³

References: [72,476–480,483]

Table S10. Calculating demand for resources compared to availability

Material	Gt of material produced	resources required	unit	% of resources produced annually that would be needed to meet demand	% of available resources needed assuming 3:1 ratio of feedstock to product
<i>Cement</i>	4.15	0.623	Gt biochar	23.95	72
<i>Aggregate</i>	21.7	21.7	Gt aggregate	1051	3154
<i>Plastics</i>	0.066	0.0429	Gt carbon	0.88	2.64
<i>Wood</i>	1.24	n/a			
<i>Brick</i>	2.4	0.162	Gt carbon	3.33	9.98
<i>Asphalt (bitumen)</i>	0.12	0.061	Gt carbon	1.25	3.76
<i>Asphalt (aggregate)</i>	2.13	2.13	Gt aggregate	103	309