# ENVIRONMENTAL IMPACTS OF MANUFACTURING CRYSTALLINE SILICON AND ORGANIC PHOTOVOLTAICS

By

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### A DISSERTATION

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#### ABSTRACT

# ENVIRONMENTAL IMPACTS OF MANUFACTURING CRYSTALLINE SILICON AND ORGANIC PHOTOVOLTAICS

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Photovoltaics (PV) should provide about 25% of the global electricity production by 2050, which will require large-scale manufacturing. PV is expected to be a clean technology that can reduce the carbon footprint of electricity production. To maximize carbon reduction and maximize the environmental benefit, we must reduce the environmental impact of the manufacturing stage. This work evaluates the life cycle environmental impact of manufacturing mature (silicon) and emerging (organic) PV and evaluates alternative processes.

For organic PV,  $C_{60}$  is often used as an acceptor material in OPV. Existing  $C_{60}$  purification methods are energy-intensive and require a large quantity of hazardous solvents. Therefore, it is desirable to modify existing  $C_{60}$  purification methods before OPV large-scale production to mitigate the potential environmental, cost, and chemical hazards of the manufacturing process. We used life-cycle assessment (LCA) to identify the environmental hotspots of the purification process. In addition to LCA, green chemistry, toxicity assessment, and analytical chemistry were employed to identify greener replacements. The alternative  $C_{60}$  purification has lower environmental (59%), cost (85%), and chemical hazard (42%) impacts compared to the existing  $C_{60}$  purification process.

For mature technologies such as silicon PV (Si PV), it is necessary to evaluate the amount of materials needed to meet the expected PV capacity additions. Si PV is 95% of the current PV market and is expected to remain the leading technology until 2040 (>50%). We estimated the

amount of material necessary for Si PV manufacturing based on PV installation in the US and the rest of the world in the next ten years. A bottom-up approach was used to evaluate the required materials for each sub-Si PV technology (e.g., aluminum back surface field, PERC, heterojunction, mono facial, bifacial, and perovskite/silicon tandem). Solar glass with 74 million metric tons and metallurgical-grade silicon (MG-Si) with three million metric tons have the highest material demand in the next decade. MG-Si production requires silica sand extracted from high-quality quartz (>98% purity). This study identified the purity and availability of potential quartz deposits globally. The country-specific carbon footprint of silica sand production was evaluated for quartz with various purity. The carbon footprint of producing silica sand was about 36% higher for low-quality quartz (65% purity) than high-quality deposits. We also quantified the carbon footprint and the cumulative energy demand of silica sand production from legal and illegal mines. The lower cost of silica sand production from illegal mines could result in using illegal quartz in the Si PV supply chain. Therefore, it is essential to have third-party certifications to ensure that the PV supply chain is free from illegal quartz and PV consumers buy ethical products.

To my lovely family! I dedicated this dissertation to all Iranians who have sacrificed their lives and times to have an independent and free country.

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## **KEY TO ABBREVIATIONS**

Al-BSF: Aluminum Back Surface Field
APAC: Asia-Pacific region
a-Si: amorphous Silicon
auq/nC <sub>60</sub> : fullerenes dispersed in water
AU: Australia
CdTe: Cadmium Telluride
CED: Cumulative Energy Demand
CIGS: Copper Indium Gallium Selenide
CS: C <sub>60</sub> Solubility
CS <sub>2</sub> : carbon disulfide
c-Si PV: mono crystalline Silicon Photovoltaic
DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene
DI water: Deionized Water
DLS: Dynamic Light Scattering
EC <sub>50</sub> : Effective Concentration
EF: freshwater aquatic ecosystem toxicity effect
EIA: U.S. Energy Information Administration
EPA: Environmental Protection Agency
ERA: Environmental Risk Assessment
FF: factor includes freshwater ecosystem exposure
GC: Gas Chromatography
GEC: Green Electronics Council

**GWP:** Global Warming Potential HPLC: High-Performance Liquid Chromatography HRTEM: High-Resolution Transmission Electron Microscopy HS: Hazardous Score IEA: International Energy Agency IRENA: International Renewable Energy Agency KH: Cambodia LC<sub>50</sub>: Lethal Concentration LCA: Life-Cycle Assessment LCC: Life Cycle Cost mc-Si PV: multi-crystalline Silicon Photovoltaic MG-Si: Metallurgical-Grade Silicon MY: Malaysia O<sup>2-</sup>: Superoxide **OPV: Organic Photovoltaic** PERC: Passivated Emitter and Rear Cell PK: Pakistan **PV:** Photovoltaic QSARs: Quantitative Structure-Activity Relationships **ROS:** Reactive Oxygen Species SG-Si: Solar-Grade Silicon SEIA: Solar Energy Industries Association SEM: Scanning Electron Microscopy

SHJ: Silicon Heterojunction
Si PV: Silicon Photovoltaic
TEST: Toxicity Estimation Software Tool
THF: tetrahydrofuran
TMB: 1,2,4-Trimethilbenznene
TU: Toxic Unit
USGS: U.S. Geological Survey
UV-VIS: UltraViolet-Visible
WD: Water Demand
WSF: Water-Soluble Fraction

XF: Freshwater ecosystem exposure

#### **Chapter 1 Introduction**

#### **1.1 Introduction**

Photovoltaics (PV) plays an essential role in decarbonizing the global energy system [1]. Fossil fuels are responsible for global warming, severely impacting the environment, economy, and public health. The transition from fossil fuels to renewables such as PV is a unique solution to mitigate global warming impacts. However, the energy transition pathway may threaten the sustainability of PV. Unsustainable manufacturing processes, using carcinogenic and hazardous materials for manufacturing PV, and using more natural resources (e.g., mining raw materials) to develop solar technologies are only a few examples of global energy transition challenges.

PV is one of the leading renewable sources of electricity production in the US and the world. Electricity was 17% of global final energy consumption in 2010 and is estimated to reach about 43% by 2050 [1]. It is expected that PV will provide about 25% of the global electricity demand by 2050 (Figure 1.1a). The total installed photovoltaic (PV) capacity is anticipated to increase from 384 GW in 2017 to 8,519 GW in 2050 [1]. PV is also the leading renewable electricity source in the US, with about 16% contribution to electricity production in 2020 and 47% in 2050 (Figure 1.2) [2]. This increase in PV installation needs manufacturing more PV and would probably increase the demand for PV materials.



**Figure 1.1.** (a) Global electricity generation from renewables and fossil fuels until 2050 and (b) global installed capacity by energy source (adapted from Global Renewables Outlook, 2020, IRENA [1])



**Figure 1.2.** The contribution of renewables and solar energy in the US electricity production until 2050 (adapted from the Annual Energy Outlook 2021, EIA, 2021 [2])

Photovoltaic is supposed to be a green and clean technology. However, the socioenvironmental impacts due to facing some challenges and limitations such as material shortage and unsustainable manufacturing processes can blemish PV's public image. In general, PV can be categorized into three groups: wafer-based crystalline silicon, thin-film, and organic [3]. Silicon PV (Si PV) and thin-film PV are well developed and are commercially available. Si PV was more than 95% of the PV market in 2020, and the rest was thin-film PV technologies (e.g., cadmium telluride (CdTe) & copper indium gallium selenide (CIGS/CIS)) [3,4]. Organic PV (OPV) is an emerging technology with a great potential market in the future due to its unique properties, such as absorbing indoor light spectrum, which makes it a suitable source of energy for indoor applications [5]. PV limitations vary from one technology to another, depending on the PV manufacturing stage. Commercialized PV technologies such as Si PV may suffer from material shortage due to market penetration and large-scale production, increasing material demand. While, for early-stage PV technologies such as OPV, limitations can be different, and challenges may relate to the manufacturing processes. Figure 1.3 explains the Collingride Dilemma for PV technologies. The freedom of design in emerging technologies (e.g., OPV) is much higher than mature PV technologies (e.g., Si PV), which means that the feasibility and modification cost can be much less for early-stage technologies. This shows the potential possibility and importance of the environmental modifications of manufacturing processes for OPV before large-scale production. On the other hand, it is essential to consider supplying materials needed for manufacturing more mature PV technology such as Si PV due to their high material demand to keep a large-scale production constant.



Figure 1.3. The Collingride Dilemma diagram for PV technologies. Data is based on the 2019 IRENA report [6].

#### **1.2 Motivation**

PV is expected to be a green replacement for fossil fuels in the next couple of decades. PV is anticipated to be a clean technology that can eliminate the greenhouse gas emission generated by fossil fuels. However, existing PV manufacturing processes are not green, and associated carbon footprints threaten PV sustainability. In addition, the socio-environmental impacts of providing materials necessary for PV production and the possibility of using illegal materials are significant challenges that can tarnish the PV image. Therefore, it is essential to evaluate the sustainability (i.e., environmental, cost, and chemical hazards) of the PV manufacturing process as well as the socio-environmental impacts of supplying PV materials.

The organic photovoltaic (OPV) manufacturing process needs a sustainable evaluation and some modifications before large-scale production. OPV has recently gained attention due to its unique advantages. OPV is cheaper, lighter, and less complex to be manufactured than traditional PV, can absorb indoor light spectrum, and can be fabricated in a larger area using colorful and flexible materials [5,7–10]. These properties make OPV desirable for interior design usages and expand OPV's applications as windows for buildings and as screens for electronic devices [11–15]. Low efficiency is the main obstacle for commercializing OPV; however, there has been a remarkable growth reported for OPV efficiency in recent years. OPV efficiency has increased from 5% in 2005 to 12% and 18% in 2015 and 2020, respectively, and is expected to grow more in the future [16–19]. Most previous studies focused on improving OPV efficiency and its mechanical durability, and only a few studies investigated the environmental impacts of synthesizing required materials for OPV. Even though fullerene ( $C_{60}$ ) is the critical material for OPV manufacturing (Figure 1.4), its production process requires a large amount of energy and hazardous materials [20,21]. Therefore, it is essential to evaluate the carbon footprint, cost, and chemical hazards of

producing fullerenes to ensure that the OPV manufacturing process remains sustainable before large-scale production.

The material shortage is a severe threat for Si PV manufacturing. Si PV was more than 95% of the PV market in 2020 and is expected to remain the primary stream (>50 %) until 2040 [6,22]. Therefore, it is crucial to quantify materials necessary to support Si PV production in the next couple of years. Most previous studies applied theoretical models on historical PV data to estimate the PV material requirement. They ignored PV technology improvements such as efficiency, market share, wafer thickness, glass thickness, etc., directly affecting the amount of required materials. Therefore, there is an essential need to project Si PV materials based on Si PV industry improvements. In addition, the socio-environmental evaluation of supplying raw materials (e.g., quartz) necessary for Si PV manufacturing was widely ignored in the literature. Therefore, the availability and the quality of global deposits for raw materials that may affect Si PV production should be carefully investigated.

#### **1.3 Background**

#### 1.3.1 Life-cycle assessment (LCA)

LCA is a systematic approach to evaluate the entire life cycle of a product or a process from raw material extraction to manufacturing, distribution, use phase, and end of life stage [23] (Fig. 1. 4a). A general LCA framework contains four main steps: goal and scope definition, inventory analysis, impact assessment, and interpretation (Fig. 1. 4b). LCA is widely used for the environmental evaluation of PV manufacturing. LCA can be applied to any stage of the PV manufacturing process to quantify associated environmental impacts such as carbon footprint (global warming potential - GWP), cumulative energy demand (CED), water footprint (WD), and E-factor to modify processes for lower impacts on the environment.



**Figure 1.4.** (a) Life cycle stages of a product or a process and (b) LCA framework (adapted from [23])

#### 1.3.2 Green chemistry principles

Green chemistry principles were introduced in 1998 (Table 1.1) [24]. Since then, it has been widely used to design chemical synthesis at early stages to avoid or mitigate the adverse issues in downstream. Green chemistry is a relatively new concept in nanomaterial synthesis for OPV. Green chemistry principles can determine alternative safer, energy-efficient, and less toxic synthesis procedures for nanomaterial production necessary for OPV manufacturing [25,26].

No.	Metrics
1	<b>Prevention</b> : It is better to prevent waste than to clean it later.
2	Atom economy: processes should be designed to maximize the number of initial atoms in final products.
3	Less hazardous chemical synthesis: processes should be designed to use and generate materials with little
	or no toxicity to the environment and human health.
4	Design safer chemicals: minimizing the toxicity of final products.
5	Safer solvents: solvents or any auxiliary materials should not be used as much as possible and should be
	nonhazardous if they are used.
6	Design for energy efficiency: energy requirements should be minimized in processes. Experiments should
	be conducted at ambient temperature and pressure.
7	Use of renewable feedstocks: Raw materials should be renewable wherever possible.
8	Reduce derivatives: unnecessary derivatizations should be avoided since they can generate wastes and
	may need more regents.
9	Catalysis: catalysis reagents are better than stoichiometric reagents.
10	Design for degradation: final products should be designed in a way to be degradable in the environment.
11	Real-time analysis for pollution prevention: analytical analysis should be used for in-process monitoring
	to control before making wastes.
12	Inherently safer chemistry for accident prevention: selected chemicals should be safer to minimize
	potential hazards due to accidental release, explosion, or fire.

Table 1.1. Twelve principles of green chemistry [27].

#### 1.3.3 Toxicity assessment

Toxicity evaluation is a powerful tool for the environmental risk assessment of chemicals [28]. The toxicity of chemicals can be quantified via theoretical models and experiments. For example, the toxicity of some chemicals, such as organic compounds, can be predicted based on theoretical models such as Quantitative Structure-Activity Relationships (QSARs). In contrast, the toxicity of other materials such as nanocarbons should be quantified based on toxicity experiments. The U.S. Environmental Protection Agency (EPA) developed the Toxicity Estimation Software Tool (TEST) using QSARs methodologies to allow users to predict chemical toxicity based on molecular structures [29]. The EPA also introduced standard protocols such as EPA600/8-87/011 for quantifying material toxicity via acute and chronic toxicity experiments [30].

The most common indicator in animal toxicity studies is the  $LC_{50}$ , which corresponds to the lowest concentration associated with a 50% death rate [31–33].  $LC_{50}$  can be used to quantify the toxicity of chemicals and compounds at early stages [34]. *Daphnia Magna*, a 0.5-5 mm-long

planktonic invertebrate organism, is recommended by EPA for toxicity assessment as a reliable representative of freshwater ecosystems at the cellular and animal scales [30,32][31]. They are easy to culture, sensitive to toxicants, and large enough to be visible under light microscopes [32,35].

# **1.3.4** Analytical chemistry and material characterization techniques for environmental assessment

Analytical chemistry instruments such as high-performance liquid chromatography (HPLC), gas chromatography (GC), UV-VIS spectroscopy, and mass spectroscopy are widely used for quantifying and analyzing chemicals in compounds. These instruments are also capable of being employed for monitoring the quality and quantity of target chemicals and by-products along with the production procedures for environmental evaluation purposes [36]. In addition, material characterization techniques such as high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), optical microscopes, and Zeta Potential Analyzer are used for characterizing nanomaterials such as fullerene ( $C_{60}$ ) to identify the size, shape, and distribution of synthesized nanoparticles to study nanomaterial impacts on the environment.

#### 1.3.5 Organic photovoltaic (OPV)

OPV can be divided into a single organic layer, bilayer (e acceptor & e donor), and bulk heterojunction (interpenetrating network of e acceptor and e donor) organic cells. A typical OPV structure includes an active organic layer containing two types of materials (e acceptor & e donor) sandwiched between two thin-film electrodes (Figure 1.5) [37]. The efficiency of single organic layer solar cells is much lower than the efficiency of bilayer organic solar cells. The low interfacial area between the donor and acceptor materials in the bilayer is an obstacle to have a commercial product with a comparable efficiency with Si PV and other types of PV technology. The bulk heterojunction is another structure in that materials are blended in a solvent before deposition on the glass layer. This technique creates an interpenetrating network of electron acceptor and electron donor that increases the interfacial area results in a higher efficiency [38]. Layer-by-layer processing is the most recent technology with the capability of manufacturing OPV on a large scale [38].



Figure 1.5. A typical structure of organic photovoltaic (OPV)

#### **1.3.6 Silicon photovoltaic (Si PV)**

Si PV manufacturing process starts from mining quartz followed by silica sand extraction, metallurgical-grade silicon (MG-Si) production, polycrystalline silicon purification, crystallization, wafering, cell processing, and module manufacturing [4]. Silica sand purity depends on the quality of quartz deposits. MG-Si purity reaches more than 99% by removing impurities from silica sand in an arc furnace at a high temperature (about 1,800 °C). Further purification requires removing impurities such as boron and phosphorus to produce solar-grade silicon (SG-Si) with 99.9999999% purity necessary for wafer production. The typical thickness of Si PV wafer is 170 µm for crystalline Si PV (c-Si PV) and 180 µm for polycrystalline Si PV (mc-Si PV) and is expected to be 50 µm by 2030 [39]. The wafer sizes change from 243 cm<sup>2</sup> (156 mm

 $\times$  156 mm) to 441 cm<sup>2</sup> (210 mm  $\times$  210 mm) [3]. A typical Si PV module area is 1.6 m<sup>2</sup> containing 60 individual cells of 243 cm<sup>2</sup> [4]. The current efficiency is 19.5% for c-Si PV and 18.0% for mc-Si PV which is expected to be 21.5% and 20% in 2031, respectively [39]. The typical structures of Si PV sub-technologies are shown in Figure 1. 6.



Figure 1.6. Silicon photovoltaic (Si PV) sub-technology structures

#### **1.4 Dissertation outline**

This dissertation aimed to evaluate the environmental impacts of OPV and Si PV manufacturing by:

- Identifying the toxicity of existing solvents used for fullerene (C<sub>60</sub>) production necessary for OPV manufacturing (Chapter 2)
- 2. Determining the environmental hotspots and alternative non-hazardous solvents for producing fullerene (C<sub>60</sub>) used for OPV manufacturing (Chapter 3)
- 3. Quantifying materials necessary for Si PV manufacturing in the next ten years (Chapter 4)

4. Analyzing the carbon footprint and cumulative energy demand of supplying silica sand needed for Si PV manufacturing (Chapter 5)

To achieve these goals, we used a combination of LCA, green chemistry, toxicity assessment, sustainability analysis, analytical chemistry, and material flow, along with scenario analysis and experiments.

The second Chapter evaluated the toxicity of existing solvents consumed for making fullerene ( $C_{60}$ ) used for OPV manufacturing. The existing solvent for the large-scale production of  $C_{60}$  is 1,2,4-Trimethilbenznene (TMB). TMB is highly toxic and carcinogenic, with a possibility of severe impacts on workers and the environment in accidental release incidents. We conducted a series of singular and combined toxicity experiments to quantify the toxicity of TMB and its potential replacements. Alternative solvents were prescreened based on  $C_{60}$  solubility and hazardous score. Linseed oil, olive oil, and sunflower oil were identified as non-hazardous alternative solvents for TMB.

The third Chapter focused on environmental, cost, and chemical hazards evaluation of using the potential alternative solvents from the second Chapter, as well as other potential solvents for  $C_{60}$  production.  $C_{60}$  purification was reported as the most energy-intensive stage in manufacturing OPV. We evaluated the environmental (GWP, CED, WD, and e-factor), cost, and chemical hazards of existing  $C_{60}$  purification methods to identify the baseline with the lowest environmental, cost, and chemical hazard impacts. LCA was used to determine the environmental hotspots of the baseline. Green chemistry principles and toxicity assessment were employed to develop a purification process using potential alternative solvents. The greener replacement for

TMB was determined for a method with the lowest environmental, cost, and chemical hazard impacts.

The fourth Chapter identified the material needed for Si PV manufacturing in the next decade. We used a bottom-up approach to evaluate the amount of materials for each Si PV sub-technologies. We estimated the amount of PV materials based on technology improvements reported in energy outlooks and the annual reports of global leading Si PV producers.

The fifth Chapter evaluated the carbon footprint of supplying raw materials necessary for Si PV manufacturing. Metallurgical-grade silicon (MG-Si) is the critical material for Si PV manufacturing. Quartz is the primary raw material needed for MG-Si production. The quartz purity is different for various mines. This can result in having extra processes to remove impurities from quartz before using it for MG-Si production. This Chapter quantified the GWP and CED of quartz mining, silica sand extraction, and MG-Si production for various countries. We determined potential quartz resources for future Si PV production and evaluated the associated carbon footprint.

Overall, this dissertation focused on the environmental assessment of manufacturing OPV and Si PV. Alternative green solvents were introduced for  $C_{60}$  production necessary for OPV manufacturing to reduce the environmental, cost, and chemical hazards of existing  $C_{60}$  production processes. In addition, solar materials needed for Si PV manufacturing were estimated for the next ten years for the US and the rest of the world. We also quantified the country-specific carbon footprint and CED of quartz mining, silica sand extraction, and MG-Si production.

# Chapter 2 Identifying alternative solvents for C<sub>60</sub> manufacturing using singular and combined toxicity assessments<sup>a</sup>

A large amount of hazardous solvents is consumed in OPV manufacturing. Fullerene ( $C_{60}$ ) is used as e acceptor/donor material in OPV. Figure 2.1 shows the process of  $C_{60}$  production, where the purification step needs a large amount of hazardous solvents to separate  $C_{60}$  from  $C_{70}$  and higher fullerenes. A well-known large-scale process for C60 purification is complexation with 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) that requires about 120 kg highly toxic solvent (1,2,4 trimethylbenzene – TMB) to produce one kg  $C_{60}$  with >99% purity. This Chapter identified alternative nontoxic solvents for TMB using green chemistry principles as well as singular and combined toxicity assessments.



**Figure 2.1** Fullerene ( $C_{60}$ ) production process. The red box shows the purification stage to separate  $C_{60}$  from  $C_{70}$  and higher fullerenes.

<sup>&</sup>lt;sup>a</sup> Parts of this chapter have been published as Seyed M. Heidari, Annick Anctil, "Identifying alternative solvents for  $C_{60}$  manufacturing using singular and combined toxicity assessments," Journal of Hazardous Materials, Volume 393, 2020 DOI: <u>https://doi.org/10.1016/j.jhazmat.2020.122337</u>

#### 2.1 Background

Fullerenes are allotropes of carbon that naturally occur in space [40,41]. However, they can also be produced under high temperature and low vacuum pressure conditions using combustion or arc plasma techniques [21]. The most stable fullerene is C<sub>60</sub>, where 60 carbon atoms form a stable hollow sphere structure [42]. Due to their unique physicochemical properties, C<sub>60</sub> fullerenes are widely used in different industrial, commercial, and medical applications, such as organic solar cells, cosmetic products, drug delivery, cancer therapy, gene delivery, and photodynamic treatment [43–49]. C<sub>60</sub> fullerenes are nontoxic. They are even sold as a human supplement because they are believed to inhibit allergic responses [50], increase hair growth [51], reduce symptoms of Parkinson's [52], promote weight loss, reduce inflammation, and increase longevity [53]. The global fullerene market was \$4.7 billion in 2016 [54] and is expected to grow by 7.9% annually until 2024 [55].

 $C_{60}$  is a nonpolar hydrophobic molecule that is soluble in petroleum-based solvents, such as benzene (2.9 g/L), toluene (8.7 g/L), o-xylene (9.3 g/L), tetralin (15.7 g/L), and 1,2,4trimethylbenzene (TMB) (17.9 g/L) [56]. Those solvents are used during various stages of  $C_{60}$ manufacturing. The purification process requires a huge amount of solvents. For instance, more than 120 kg of TMB per kg of  $C_{60}$  is used during the fullerene production to separate  $C_{60}$  from  $C_{70}$ and higher fullerenes when using the complexation method [57,58]. Finding a greener solvent before large-scale production could reduce the impact of an accidental spill. Green chemistry principles can be used to select alternative solvents to reduce the environmental impacts of industrial nanomaterial production processes [59–62]. Green chemistry use principles to eliminate or mitigate the use or generation of hazardous materials in the design, manufacturing, and use phase of chemicals. It addresses three main categories: toxicity, material efficiency, and energy efficiency [63–66]. In this Chapter, plant-based solvents (essential oils) were considered as potential alternative solvents since they are nontoxic [67], and their solubility with  $C_{60}$  is similar to that of conventional solvents such as TMB (Table A1 in Appendix A).

Investigating the potential toxicity of chemicals is required for a green chemical design [66,68]. The most common indicator in animal toxicity studies is the EC<sub>50</sub>, which corresponds to the lowest concentration associated with a 50% death rate [31–33]. The EC<sub>50</sub> of fullerenes prepared in organic solvents such as toluene, acetone, and tetrahydrofuran (THF) varies from 0.4 to 0.8 mg/L [69–72]. The toxicity in those solvents is due to the residual solvent attached to the fullerene structure [73]. To avoid using organic solvents, fullerenes can be dispersed in water (auq/nC<sub>60</sub>) by mixing the solution for two to eight weeks using magnetic stirring. Using this method, the C<sub>60</sub> toxicity is lower. In one study, less than 20% of the daphnids died when exposed to a ten mg/L auq/nC<sub>60</sub> solution [74]. In two other studies, neither acute (48 h) nor chronic (21 days) toxic impacts were reported for daphnids exposed to 35 mg/L auq/nC<sub>60</sub> [75,76]. Table A2 provides additional details about previous toxicity studies for C<sub>60</sub> in water and other solvents.

Life-cycle assessment (LCA) is an established method to evaluate the environmental impact of a product. However, its use for nanomaterials and the quality of published studies have been criticized due to the lack of toxicity characterization factors [77]. The recommended method for LCA toxicity impact is the consensus model USEtox developed by the UNEP/SETAC [78]. This model uses an ecotoxicological characterization factor to predict the ecotoxicity impacts of a chemical in freshwater ecosystems. This factor includes environmental fate (FF), freshwater ecosystem exposure (XF), and freshwater aquatic ecosystem toxicity effect (EF) [79]. Environmental risk assessment (ERA) is an approach to characterize the magnitude of health risks from contaminants and predict the probability of adverse health effects of hazards on humans and

the environment [28,80,81]. The  $EC_{50}$  from single toxicity experiments is used for characterization factors in LCA [82] and ERA studies [28].

Although previous studies characterized  $C_{60}$  as a nontoxic nanocarbon, the assessment is incomplete because it ignores the combined toxicity of fullerenes and solvents. Focusing only on the toxicity of each chemical to identify an alternative solvent is not adequate since the interactions between chemicals may affect the overall toxicity. Previous toxicological studies on chemical mixtures showed that singular toxicity could be different from combined toxicity, and the effects of interactions could be antagonism, additive, or synergism [83-89]. Even though C<sub>60</sub> and the selected essential oils are non-toxic, using essential oils as solvents could facilitate the fullerene transport into biological systems, in a process analogous to that observed in quantum dots and linseed oil [90]. Previous research demonstrated that nC<sub>60</sub> molecules could destabilize cell membranes through a variety of mechanisms [91–94] and cause membrane leakage that kills cells [95]. Furthermore,  $nC_{60}$  that have entered the biological systems can be photoactivated due to their  $\Pi$  conjugation and generate superoxide anions that are toxic to cells [90,96,97]. The photoactivation effect is used for medical applications to kill cancer cells or HIV viruses [98–100]. Therefore, the combination of C<sub>60</sub> and essential oils, which are both nontoxic materials, is potentially toxic to the environment and needs to be investigated.

In this Chapter, We used *Daphnia magna*, a 0.5-5 mm-long planktonic invertebrate organism recommended by the US EPA for toxicity assessments [30,32]. It is a reliable representative of freshwater ecosystems in singular and combined toxicity assessments at the molecular, cellular, and animal scales [32,101–103]. Daphnids are sensitive to toxicants, large enough to be visible under light microscopes, abundant in the northern hemisphere, and easy to culture [32,35]. They are also recommended as an alternative to mammals in prescreen chemical

toxicity studies since these microcrustaceans are at the basis of the freshwater ecosystem food chain [31].

The objective of this Chapter was to identify a suitable replacement for TMB, which is used in large quantities for  $C_{60}$  manufacturing, by using singular and combined toxicity assessments. Singular toxicity tests were designed to quantify the toxicity of  $C_{60}$ , TMB, and alternative solvents. Combined toxicity tests were used to investigate the effect of interactions of  $C_{60}$  and the selected solvents on *D. magna*. This work will contribute to understanding the importance of combined toxicity assessments in environmental studies such as solvent selection using green chemistry, life-cycle assessment, and environmental risk assessments where toxicity evaluations mostly rely on singular toxicity and ignore combined toxicity.

#### 2.2 Material and methods

The experimental plan was designed to quantify the singular and combined acute effects of  $C_{60}$  with different solvents (TMB, linseed oil, olive oil, and sunflower oil) on *D. magna*. The concentrations of  $C_{60}$  and solvents were determined based on prescreen-test results.

#### 2.2.1 Daphnia magna

*Daphnids* were obtained from an EPA-verified laboratory in Colorado (Aquatic BioSystem Inc.) and cultured in our laboratory in 2-L glass beakers for 3-5 weeks under the recommended conditions [30] (Figure A1). Briefly, *daphnids* developed in reconstituted water [30] at room temperature (20±1 oC) and were fed (5 mg/L trout food and 108 cells/L Raphidocelis subcapitata algae) three times per week. Fluorescent light with an intensity of 70±5 foot candles was used for a 16 h photoperiod. The alkalinity, hardness, and pH of reconstituted water were measured using water quality test stripes (McMaster-Carr Supply Company) and a pH meter (VWR SympHony

Benchtop Meter B10P) to ensure that they were within the EPA-recommended ranges. Offspring *daphnids* (< 24 h) were used for acute tests. Adults were separated from young *daphnids* one day before the experiments to ensure that all *daphnids* for acute tests were less than 24 h old. Five *daphnids* were exposed to toxicants in four 100 mL glass beakers (20 *daphnids* for each concentration) in all experiments. The acute toxicity experiments were valid based on the EPA protocol since the percentage of dead *daphnids* was less than 10% in controls [30].

#### 2.2.2 Solvents

Potential alternative solvents were selected based on green chemistry principles, in particular, waste minimization and selection of less hazardous solvents (Principles #1 and 3). The solvents were selected based on the C<sub>60</sub> solubility and hazardous score as calculated by Lee [104] (Tables A1 and A3) Linseed oil (CAS 430021), olive oil (CAS 01514), sunflower oil (CAS 530285), and TMB (CAS T73601) were purchased from Sigma Aldrich (Burlington, MA). Preparation of solvents' stocks followed a previously-reported procedure by which aromatic hydrocarbons and crude oil were added to water and stirred for 24 h to reach stability [105–107]. In summary, 280 g of each essential oil and one g of TMB were added separately to 1-L Erlenmeyer flasks and filled up to one L with reconstituted water to minimize the headspace and avoid losing potential volatile components. Solutions were stirred on a magnetic stir plate for 24 hours (480 rpm) at room temperature. All flasks were sealed by parafilm sealing and covered by aluminum foil to avoid evaporation, oxidation, and photodegradation. Since the solubility of essential oils and TMB in water is low (Table A1), solutions were left for one h. The undissolved fraction was removed from the top, and the water-soluble fraction (WSF) was collected at the bottom using a separatory funnel. The composition of WSF was determined using an Agilent 7890B gas chromatograph/ triple quadrupole mass spectrometer 7010B (GC-MS, Agilent, Santa

Clara, CA). The GC-MS method is described in Appendix A (A9). The average and standard deviation of calculated numbers were based on analyzing the quadruplicate of each WSF.

#### 2.2.3 Preparation and characterization of fullerene

C<sub>60</sub> fullerenes with 99% purity were purchased from MER (Tuscan, AZ). Fullerene stocks were prepared by adding 250 mg of C<sub>60</sub> into 1 L of reconstituted water and stirred for two weeks at ambient temperature to reach stability [108]. The fullerene stock was prepared in a nitrogen atmosphere and covered with aluminum foil to minimize fullerene oxidation or photodegradation. The concentration of suspended fullerenes in the solution was verified using a UV-VIS spectrophotometer (SHIMADZU, UV-2600 120V) based on the measured absorption at 335 nm. Fullerene was extracted in accordance with a previously reported method [109]. Briefly, 2% sodium chloride in deionized water and toluene (HPLC grade) were mixed for 2-3 minutes with fullerene-containing water using a 2:2:1 ratio (C<sub>60</sub> solution: toluene: 2% sodium chloride) followed by three washes with toluene to ensure that all fullerenes were dissolved in toluene. A plastic pipette was used for UV-VIS spectroscopy measurements to collect the top layer, which contained fullerenes dissolved in toluene. After stirring for two weeks, the morphology of suspended fullerenes was determined using ultra-high-resolution transmission electron microscopy (HRTEM) (JEOL USA JEM-2200FS TEM) at 200 kV. Samples were placed on 300-mesh copper carbon grids and dried before imaging. The surface charge and size of suspended fullerenes in reconstituted water after stirring for two weeks and the test mediums were measured using dynamic light scattering (DLS) (ZetaPALS, Brookhaven Instruments Corporation). Quadruplicates of each test medium were used to calculate the average and standard deviation.
## 2.2.4 Toxicity experiments

Prescreen tests were designed to determine the appropriate acute-test concentration range for EC<sub>50</sub> calculation and a dose-response curve. For TMB, 8, 0.8, and 0.08 mL of WSF and for essential oils, 24, 8, and 0.8 mL of WSF were added separately to 100-mL glass beakers and filled up to 80 mL with reconstituted water. Five young *daphnids* were transferred one by one to each beaker using a plastic pipette and exposed to toxicants for 48 h. The number of dead *daphnids* was counted after 48 h (Table A4). The concentration range of toxicants for acute tests was established using the lowest concentration with 100% *daphnids* death and the highest concentration with 0% death. Five concentrations of linseed oil (138, 69, 34.5, 17.25, and 8.625 g/L), six concentrations of olive oil (276, 138, 69, 34.5, 17.25, and 8.625 g/L), seven concentrations of sunflower oil (552, 276, 138, 69, 34.5, 17.25, and 8.625 g/L) and eight concentrations of TMB (1539, 1000, 650, 422.5, 274.6, 178.5, 116, and 75.4 mg/L) were prepared by diluting WSF with reconstituted water for acute tests.

As summarized in Table 2. 1, the acute tests followed the EPA protocol (600/8-87/011 1986) [30] for all nine experiments plus the control. Briefly, young daphnids (< 24 h) were exposed to at least five concentrations (20 *daphnids* in four beakers for each concentration) under the fluorescent light (16 h period) and at room temperature for 48 h. The average number of dead (or immobilized) *daphnids* after 48 h was used for the dose-response curves to extrapolate the EC<sub>50</sub> of each toxicant. The fixed ratio design approach was used to prepare the mixture of C<sub>60</sub> and solvents, as described in similar combined toxicity studies [86,88,89,110–113]. Tests were designed to evaluate the interaction of C<sub>60</sub> with the various solvents using 1 toxic unit (TU) as the reference. For the solvent, one TU was the EC<sub>50</sub> concentration, and for C<sub>60</sub>, it was the maximum concentration (176 ppm). Six different solutions were prepared where the concentration of solvent

was kept constant at 1 TU (e.g., 1 TU for olive oil was 54,485.4 ppm) and the C<sub>60</sub> concentration was varied from 0 to 1 (0, 0.0625, 0.125, 0.25, 0.5, and 1) [84]. For TMB and C<sub>60</sub>, as suggested in the literature for situations with a large difference in toxicity [83,87], a concentration lower than the EC<sub>50</sub> was used. Using a lower concentration than the EC<sub>50</sub> for TMB allows us to evaluate the development of toxic responses due to changes in C<sub>60</sub> concentration. The average and standard deviation for the EC<sub>50</sub> were calculated with a 95% confidence interval using OriginLab (version 2018) software. After 48 hours of exposure to toxicants, morphology changes in the daphnids were identified using a light microscope (Olympus BH2-RFCA). After transfer from the media to microscopy slides, the daphnids' heartbeats were counted visually three times for 15 seconds intervals per *D. magna* [114–116].

# 2.3 Results and discussion

# 2.3.1 Essential oil prescreening

As highlighted by the purple box in Figure 2.2, potential alternative solvents were identified based on their high  $C_{60}$  solubility (CS) and low hazardous score (HS) compared to TMB. Cedar oil was eliminated due to its high hazardous score (HS=1.33), which is the same as TMB. In contrast, linseed oil (HS=0.33, CS=53.1 g/L), olive oil (HS=0.67, CS=23.6 g/L), and sunflower oil (HS=0.33, CS=6.91 g/L) were selected as potential alternative solvents for toxicity assessments. In Figure 2.2, hazardous score and  $C_{60}$  solubility were normalized based on the hazardous score from toluene and the  $C_{60}$  solubility of linseed oil because they were the highest value for each category.

	Experime Toxi		Concentration		
	nts				
Singular (S)	$S_1$	C <sub>60</sub>	176, 88, 44, 22, and 11 mg/L		
	$S_2$	TMB	1539, 1000, 650, 422.5, 274.6, 178.5, 116, and 75.4 mg/L		
	<b>S</b> <sub>3</sub>	Linseed oil	138, 69, 34.5, 17.25, and 8.625 g/L		
	S4	Olive oil	276, 138, 69, 34.5, 17.25, and 8.625 g/L		
	<b>S</b> <sub>5</sub>	Sunflower oil	552, 276, 138, 69, 34.5, 17.25, and 8.625 g/L		
	Control	Reconstituted water			
		Toxicants (40 mL of solvent solution + 40 mL of auq/nC <sub>60</sub> )			
Combined (C)	C1	TMB $(EC_{50}) + C_{60} (S_1)$			
	C <sub>2</sub>	Linseed oil $(EC_{50}) + C_{60} (S_1)$			
	C <sub>3</sub>	Olive oil $(EC_{50}) + $	$C_{60}\left(\mathbf{S}_{1} ight)$		
	C4	Sunflower oil (EC5	$C_{60} + C_{60} (S_1)$		
`	Control	40 mL of solvent a	t EC <sub>50</sub> + 40 mL of reconstituted water		

Table 2.1. Singular and combined toxicity assessment of different experiments.



**Figure 2.2.** Hazardous score and  $C_{60}$  solubility of petroleum-based and plant-based (essential oils) solvents compared to the baseline (TMB). Potential alternative solvents are located in the purple box.

# 2.3.2 Singular toxicity assessment of C<sub>60</sub> fullerenes

The morphology of  $C_{60}$  in auq/n $C_{60}$  suspensions was evaluated using HRTEM and is presented in Figure 2.3. The TEM images of auq/n $C_{60}$  show that after two-week stirring, n $C_{60}$  were present in both individual ( $\approx$  7 nm) and agglomerated (7 nm - 1 µm) forms. Fullerenes can naturally aggregate and form larger fullerene particulates after release into water systems [117]. Therefore, size screening was not used to remove particulates larger than 200 nm because this could naturally occur in the environment. Table 2. 2 presents the average surface charge and size of agglomerated fullerenes in different solvents. Based on the zeta potentials results, fullerenes were moderately stable in all test mediums [118].

Media	Average size (nm)*	Zeta potential (ξ, mV)	
Deionized water	131	- 38.8	
Reconstituted water (auq/nC60)	$539 \pm 177$	$-38.5\pm0.2$	
$C_1 (TMB + auq/nC_{60})$	$449\pm285$	$-38.2\pm0.3$	
$C_2$ (Linseed oil + auq/n $C_{60}$ )	$318 \pm 127$	$-38.4 \pm 0.3$	
$C_3$ (Olive oil + auq/nC <sub>60</sub> )	$470 \pm 171$	$-38.3\pm0.2$	
$C_4$ (Sunflower oil + auq/nC <sub>60</sub> )	$457 \pm 276$	$-38.3\pm0.3$	

 Table 2.2. Physiochemical properties of suspended fullerenes (88 ppm)\* in the test medium.

\* Table A5 provides more information on physiochemical properties of suspended fullerenes at the minimum and maximum concentrations

The concentration of  $C_{60}$  in the fullerene stock and dilutions was verified by measuring the absorption at 335 nm in UV-VIS spectroscopy (Figure A2). Stable  $C_{60}$  suspension was reported for concentrations lower than five mg/L [74]. However, concentrations as high as 176 mg/L were used to find the EC<sub>50</sub> of  $C_{60}$  in this study.



**Figure 2.3**. Auq/nC<sub>60</sub> morphology after stirring for two weeks at room temperature in the absence of light and oxygen. (a) agglomerated  $nC_{60}$ , (b,c) the distribution of nanoscale  $nC_{60}$  in stock with different sizes, and (d) an ultra-high-resolution image showing the existence of a pristine C<sub>60</sub> molecule.

All concentrations of  $auq/nC_{60}$  were not toxic to *daphnids*, as demonstrated by the low daphnids mortality (< 20%), steady heartbeats, and unchanged morphology (Figure 2.4.) A 15% average death rate was recorded for the highest C<sub>60</sub> concentration (176 ppm), while death rates were lower than 10% at lower concentrations. Since the percentage of dead daphnids was too low to obtain the dose-response curve, which is needed to extrapolate the EC<sub>50</sub> of C<sub>60</sub>, EC<sub>50</sub> was assumed to be higher than 176 ppm. Our result was five times higher than the previous study [75], but there were also multiple differences in the experimental methods. The main differences are that they used a 10-day chronic test, the  $C_{60}$  was mixed in miliQ water for one month, and the initial C<sub>60</sub> concentrations in the test medium were different. Heartbeats were measured after 48, 72, and 96 h of exposure to auq/nC<sub>60</sub> (Figure 2.4b) to understand the long-term impacts of  $C_{60}$  on daphnids. The measured average heartbeats changed depending on the time of measurements. For the measurement after 48 hours, the heartbeats increased with increasing concentration. For the measurements at 72 and 96 hours, the trend was the opposite, with heartbeats decreasing with increasing concentration. The difference after a longer period of time could indicate chronic toxic impacts of C<sub>60</sub>, but further tests would be required to draw this conclusion. Additionally, there was no significant change in *daphnids* morphology after 48 h of exposure to different concentrations of auq/nC<sub>60</sub> compared to the control (Figure A3). At the end of the experiment, the pH was between 8.2 and 8.6.



**Figure 2.4.** (a) The average number of dead *daphnids* and pH after 48 h acute tests for different concentrations of auq/nC<sub>60</sub> and (b) heartbeats of *daphnids* after 48 h (blue triangle), 72 h (black square), and 96 h (red circle) of exposure to different auq/nC<sub>60</sub> concentrations.

# 2.3.3 Singular acute toxic impacts of solvents on daphnids

The conditions for the singular acute toxic assessment are summarized in Table 2. 1. The alternative solvents showed lower toxic impacts on *daphnids* than the baseline (TMB). Figure 2.5b and Figure A4 show the dose-response curves for the baseline and alternatives. TMB had the highest toxicity ( $EC_{50}$ = 707.8±166.0 mg/L) and sunflower oil the lowest ( $EC_{50}$  =159,920.7 ± 27,529.2 mg/L) (Figure 2.5b). The toxicity of olive oil ( $EC_{50}$ = 54,485.4±7,645.1 mg/L) and linseed oil ( $EC_{50}$  = 17,358.2 ± 6.4 mg/L) was significantly lower than the baseline (TMB). Figure 2.5c shows the *daphnids* ' morphological change after exposure to TMB and alternative solvents. There were no significant changes for daphnids in essentials oils compared to the control, but TMB seems to cause torsion in the gut and body.



**Figure 2.5.** Mortality of daphnids in singular toxic experiments after 48 h exposure to toxicants. (a) Dose-response curve of *daphnids* exposed to TMB (red), linseed oil (black), olive oil (blue), and sunflower oil (green), (b)  $EC_{50}$  of baseline versus alternative solvents, (c) morphology of *daphnids* exposed to baseline C<sub>3</sub>, alternative solvents C<sub>4</sub>-C<sub>6</sub> compared with the control C<sub>2</sub> and culture C<sub>1</sub>. The average % of dead *daphnids* with a 95% confidence interval was used for (a) and (b).

Although the  $EC_{50}$  levels calculated in this work were very high, it is possible that such concentrations would also be released in a freshwater environment. An accidental spill of concentrated fullerenes could happen for various reasons.  $C_{60}$  is dissolved in olive oil and sunflower oil at high concentrations when used as a human supplement. High concentration release in the freshwater environment could happen during manufacturing, but more likely during the transportation and use phase of the product. Fullerenes in a variety of solvents are considered safe and can be bought directly from a variety of sources, including Amazon, research groups, and healthcare companies [119–127]. There is an increased chance of improper disposal in the environment of products that are considered safe for humans [128]. For other applications, release in the environment is more likely to occur during the manufacturing stage. The purity of  $C_{60}$  depends on the application. Solar cells require very high purity, while for composite applications,

for example, the purity requirement is much lower. The manufacturer could transport lower grade material in solution before repeating the purification process to increase the purity of  $C_{60}$ . For the intermediate manufacturing stage, the transport of  $C_{60}$  in solvents is cheaper since the solvent does not need to be removed and the fullerenes dried to make a powder.

The toxicity of TMB, like other organic petroleum-based solvents, depends more on its water solubility than its chemical structure [129]. Essential oils are not miscible in water. Therefore, water solubility cannot explain the difference in toxicity. The composition of WSF from essential oils is shown in Table 2. 3 and Figure A5-7. The antioxidant production capability of essential oils seems to affect the toxicity of essential oils. Linseed oil was found to be more toxic than olive oil, which was more toxic than sunflower oil. On the other hand, sunflower oil is a stronger antioxidant than olive oil, while linseed oil produces reactive oxygen species [130–132].

		fatty acids			
Solvent	Total Concentration of	Saturated	Unsaturated fatty acids (%)		
Solvent	fatty acids (mg/L)	fatty acids (%)	Monounsaturated	Polyunsaturated	
Linseed oil	$575.42 \pm 69.35$	$10.83\pm0.81$	$75.01 \pm 1.63$	$14.17\pm2.89$	
Olive oil	Under the detection limit	$52.81 \pm 8.37$	$42.98 \pm 8.38$	$4.21 \pm 1.22$	
Sunflower oil	$2,134.12 \pm 1,412.74$	$12.53 \pm 6.94$	$45.32 \pm 1.27$	$42.14 \pm 8.19$	

Table 2.3. The water-soluble fraction composition for different essential oils

#### 2.3.4 Combined toxic impacts on daphnids

The mortality of *daphnids* in combined toxicity experiments differed from singular toxicity experiments (Figure 2.6). For the combined toxicity, the control was 40 mL of solvent plus 40 mL of reconstituted water. Different concentrations of  $auq/nC_{60}$  were used to investigate the impacts of  $C_{60}$  on the toxicity of solvents. In general, a higher concentration of  $C_{60}$  increased the mortality of *daphnids* for all combined experiments (Table 2. 1, C1-C4). For the mixture of  $C_{60}$  and linseed oil, the combined toxicity was higher for all  $C_{60}$  concentrations compared to the control (only

linseed oil). For the mixture of  $C_{60}$  and olive oil or sunflower oil, similarly to what was observed for the mixture of  $C_{60}$  and TMB, the addition of  $C_{60}$  initially reduced the toxicity of the solvent. At higher  $C_{60}$  concentrations, the toxicity exceeded the control.

The antagonism and synergism effects of  $C_{60}$  on solvents are available in Appendix A, Table A6. For TMB, the addition of  $C_{60}$  at 11 ppm reduced the toxicity of TMB while the mortality of *daphnids* did not change at concentrations between 11 and 88 ppm and increased from 5% to 20% at 176 ppm. For olive oil, the addition of  $C_{60}$  reduced the mortality of daphnids from 33% to 13% at 11 and 22 ppm and to 20% at 44 ppm, while mortality did not change at 88 ppm and increased to 40% at 176 ppm. For sunflower oil, the addition of  $C_{60}$  reduced the mortality of daphnids at 11 ppm while it did not change at 22 ppm and increased after 44 ppm.

The morphology of *daphnids* after 48 hours of exposure to combined toxicants is presented in Figure 2.6e. The deformity was observed in *Daphnids* as abnormal antennae (e.g., Figure 2.6 e5), carapace (e.g., Figure 2.6 e5), and curved spine (e.g., Figure 2.6 e6). For TMB, fullerenes were aggregated in the *D. magna's* gut, as shown in Figure 2.6 e2-e3, while for essential oils, the presence of fullerenes inside and/or outside of *daphnids* varied based on the concentration of  $C_{60}$ (Figure 2.6 e5, e6, e8, e9, e11, and e12). For essential oils with the lowest  $C_{60}$  concentration (11 ppm), there was no fullerene observed inside the *daphnids*, while, for linseed oil and sunflower oil, sticky compounds containing fullerenes were observed on the surface of *daphnids*. For essential oils with the highest  $C_{60}$  concentration (176 ppm), fullerenes were observed inside and outside the *daphnids* (Figure 2.6 e9 and e12). The pH was measured at the end of each experiment, as a pH lower than 5 is toxic for *daphnids* [130].



**Figure 2.6.**The pH of the test medium at the end of each experiment and the average mortality of *daphnids* for the acute combined toxicity experiments. *Daphnids* were exposed to (a) TMB + auq/nC<sub>60</sub>, (b) linseed oil + auq/nC<sub>60</sub>, (c) olive oil + auq/nC<sub>60</sub>, and (d) sunflower oil + auq/nC<sub>60</sub>. The average mortality of *daphnids* exposed to the control (50% solvent and 50% reconstituted water) for each mixture is shown in the red box. The average percentage of dead *daphnids* with 95% confidence intervals was used for (a)-(d). (e) The morphology of *daphnids* after 48 h of exposure to combined toxicants (C<sub>60</sub> + solvents) and controls (reconstituted water +solvents). In figure captions, water = reconstituted water.

For all the combined toxicity experiments, the higher concentrations of  $C_{60}$  increased the mortality of *daphnids* (Figure 2.6 a-d). The physiochemical properties of fullerenes, such as surface charge and particle size (Table 2.2), showed that the nano-properties were not the only reason for their toxicity. While the light microscopic images did not provide enough details to establish their exact location, at high concentrations,  $C_{60}$  were observed both inside and outside of the *D. magna* (Figure 2.6 e6, e9, and e12). The increased toxicity with increasing  $C_{60}$  concentration can be explained by two different effects, depending on whether the fullerene could reach the interior of the *D. magna* or not. Fullerenes are known to be photosensitizers [96] that can be photoactivated in the presence of oxygen and generate reactive oxygen species, such as superoxide anions, hydroxylic radicals, hydrogen peroxides, and singlet oxygens, all of which cause oxidative stress in the cell structure [131,132]. Photooxidation mostly happens outside of the cell since the

cell absorbs some parts of the wavelengths required for photoactivation [97]. If fullerenes did not enter the *D. magna*, the increasing concentration of  $C_{60}$  at the surface of the *D. magna* and the production of reactive oxygen species due to light exposure could increase the *D. magna* deaths. If fullerenes were able to reach the inside of the cells, the generation of singlet oxygens species from the oil could cause lipid peroxidation, which is toxic to the cell [133]. A low concentration of  $C_{60}$  reduced the mortality of *daphnids* in olive oil (Figure 2.6 c) and sunflower oil (Figure 2.6 d) but increased for linseed oil. The increased toxicity in linseed oil could be due to the immobilization of the *D. magna*. For the other two essential oils, the low fullerene concentration at the surface of the *daphnids* was not enough to cause death by photooxidation. Fullerenes are also known to have antibacterial properties [95,108,134] that could have helped daphnids overcome the oxidative stress from generated singlet oxygens.

Environmental oxidative stresses (internal or external) can disturb the self-regulation of reactive oxygen species (ROS) in cells, which leads to an imbalance in ROS production and the cell's ability to detoxify reactive intermediates [135–137]. Superoxide ( $O^{2-}$ ) is a normal byproduct of energy production in cells [138,139]. The superoxide leaks out of the mitochondria and is converted into hydrogen peroxide ( $H_2O_2$ ) inside the cell [139,140]. Under normal conditions, enzymes, such as catalase and superoxide dismutase, convert  $O^{2-}$  and  $H_2O_2$  to  $H_2O$  and  $O_2$  and reduce the damage to the cell [141]. Previous work showed that  $C_{60}$  could pass through the cell membrane and cause oxidative stress [142]. In this work, normal conditions might remain stable at low  $C_{60}$  concentrations. With an increase in  $C_{60}$  concentration, smaller oxidative stress might initially cause a small disturbance that cells were able to tolerate. With a further increase in  $C_{60}$  concentration, moderate oxidative stress would likely provoke apoptosis [137]. Finally, at higher  $C_{60}$  concentrations, the resulting oxidative stress might be severe enough to cause necrosis in cells

due to high environmental oxidative stress. Our work shows that singular toxicity can differ from combined toxicity assessments for  $C_{60}$ , depending on the solvent. Therefore, results from singular toxicity should not be used for LCA and ERA as it is commonly done for nanomaterials. Additional work is required to calculate the EC<sub>50</sub> of the C<sub>60</sub>-olive oil combination and used it in the LCA of fullerene purification.

This study evaluated linseed oil, olive oil, and sunflower oil as replacements for TMB in fullerene manufacturing. All of the essential oils were found to have lower singular toxicity than TMB. This work also evaluated combined toxicity, which was ignored in previous solvent selection studies that used green chemistry principles. Olive oil was selected as a non-hazardous solvent for fullerene production since its interactions with fullerenes decreased the singular toxic effects on *daphnids*. There is a rapidly growing market for fullerenes, and at this stage, finding a safe alternative solvent for their manufacturing could reduce the harmful impacts of an accidental spill. While olive oil seems to be an acceptable solvent, additional work is needed to adapt current purification methods for olive oil due to the difference in viscosity and boiling point. Though the toxicity of fullerenes is well known and has been characterized alongside many organic solvents, it has yet to be examined alongside essential oils, which are ubiquitous dietary supplements. Additional work is required to better understand the impact of fullerene concentration on toxicity and identify the exact location of fullerenes in *daphnids*.

# 2.3.5 Acknowledgment

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# Chapter 3 Environmental, cost, and chemical hazards of using alternative green solvents for C<sub>60</sub> purification

 $C_{60}$  is widely used in emerging technologies such as organic photovoltaic (OPV). However, existing purification processes require a large amount of toxic solvents such as 1,2,4trimethylbenzene (TMB). Identifying an alternative green purification process before large-scale production can reduce the environmental impact of OPV. This Chapter evaluated existing fullerene purification methods, including chromatography, crystallization, and complexation, to identify the baseline process with the lowest environmental, cost, and chemical hazard impacts. We used lifecycle analysis, green chemistry principles, and toxicity assessments as environmental engineering decision-making tools to develop a replacement for the baseline via an iterative approach. Introduction

Fullerene ( $C_{60}$ ) has gained remarkable attention due to its unique physicochemical properties, such as high chemical reactivity, making it a desirable material to associate with various compounds [143].  $C_{60}$  can also be an electron donor or acceptor in donor-acceptor systems [144]. Its industrial uses include solar photovoltaics and lasers [145]), drug delivery and cancer therapy [99], cosmetic products [146], and human supplements. Fullerenes come from the combustion of hydrocarbons under reduced oxygen conditions to produce fullerene-containing soot [147]. After separation of the fullerenes from the soot, purification is required to increase the purity of  $C_{60}$ ,  $C_{70}$ , and higher fullerenes, depending on the application. However, purification was identified as the most energy-intensive stage of making  $C_{60}$  [21], which requires a large amount of toxic solvents that may increase the environmental impacts of  $C_{60}$ .

The principal  $C_{60}$  purification methods are chromatography, crystallization, and complexation [143]. The stationary phase contains alumina, silica gel, and activated carbon for chromatography, and the mobile phase is toluene, o-xylene, or hexane, depending on the target material [148–155]. Various materials have different affinities to the stationary phase, which causes the separation of target materials from the rest. The purification yield for  $C_{60}$  with 99% purity was about 50% using chromatography [150,156]. However, the chromatography technique is time-consuming and limited by the capacity of the column and the low  $C_{60}$  solubility of solvents. In addition, it requires a large amount of stationary phase and mobile phase, increasing the cost and carbon footprints of the purification process [143]. Another drawback is the irreversible absorption of  $C_{60}$  by the stationary phase, which reduces the purification yield [150].

The crystallization method requires large amounts of solvents and energy. Crystallization is based on the different solubility of  $C_{60}$ ,  $C_{70}$ , and higher fullerenes at specific temperatures [157,158]. For example, crystallization can be used to separate fullerenes in xylene since the solubility of  $C_{60}$  is maximal at 30 °C and decrease with increasing temperature, while the solubility of  $C_{70}$  increases continuously from -20 to 90 °C [157]. Crystallization temperatures were reported at 110 °C for the  $C_{60}$ -containing solution and -16 °C for the  $C_{70}$ -containing solution [158]. A large amount of energy is required to either cool the solution to -20 °C or warming up to 90 °C, which is not recommended based on the 6th principle of green chemistry (design for energy efficiency). High purity (>99%) cannot be achieved in a single step, and therefore the crystallization process is repeated multiple times. Two crystallizations are required for  $C_{60}$  to reach 99% purity [158]. The  $C_{60}$  production yield was about 67%.

In the complexation method, lewis acids such as AlCl<sub>3</sub> were used to form a complex with  $C_{70}$  and higher fullerenes in carbon disulfide (CS<sub>2</sub>), while  $C_{60}$  was left in solution [159]. The

production yield of 99% C<sub>60</sub> was 76%, which is higher than chromatography and crystallization. However, the high affinity of AlCl<sub>3</sub> to water limits the choice of alternative solvents for the highly Other toxic  $CS_2$ . studies proposed using а bicyclic amidine, typically 1.8-Diazabicyclo[5.4.0]undec-7-ene (DBU), to selectively form a complex with fullerene following the complexation order of  $C_{70}$ ,  $C_{70}$ , and  $C_{60}$  [58,160]. They were able to extract 76% of  $C_{60}$  with 99% purity at a large scale and retrieve C<sub>70</sub> and higher fullerenes. However, this process requires a large amount of toxic solvents such as 1,2,4-trimethylbenzene (TMB).

Life-cycle assessment (LCA), green chemistry, and toxicity assessment are widely used to reduce the environmental impacts of the nanomaterial synthesis process. LCA is a systematic method used to evaluate the potential environmental effects of products and procedures during their life cycle [77]. LCA has been used to quantify the global warming potential (GWP) and cumulative energy demand (CED) of carbon nanomaterial's environmental impacts [161–164]. Green chemistry is a decision-making tool to design chemical products and processes to reduce using and generating hazardous materials [66]. Green chemistry principles were proposed to maximize the production rate and minimize adverse impacts of nanomaterial production [165,166]. Toxicity assessment is to measure the actual effects of materials on the environment [167]. It was employed as a decision-making tool to identify potential replacements for toxic solvents used for  $C_{60}$  production [168]. A previous study on fine chemical production proposed a framework based on an iterative approach using green chemistry principles and life cycle analysis to determine alternative methods with lower environmental, cost, and chemical hazard impacts [104].

Existing  $C_{60}$  purification methods require a large amount of hazardous solvents. This Chapter used LCA, green chemistry principles, and toxicity assessments to identify green alternative solvents for  $C_{60}$  purification. First, we determined the baseline process with the lowest environmental, cost, and chemical hazard impacts among existing  $C_{60}$  purification methods. Then we used LCA to identify the environmental hotspots of the baseline. Next, green chemistry and toxicity assessments were employed to determine potential alternative solvents for the baseline. LCA, green chemistry principles, and toxicity assessments were used continuously to modify the baseline via an iterative approach to determine a  $C_{60}$  purification process with less environmental, cost, and chemical hazard impacts than the baseline.

The original idea for this Chapter was from Eunsang Lee, who conducted the environmental and cost impact assessment of existing purification methods. I quantified the amount of materials needed for each existing purification process and calculated the hazardous score of each method. Ben Cecil contributed to the life cycle cost calculation. He compiled the price of energy materials based on my life cycle inventory analysis (Table B7). I provided the production rate (Table B6), and he conducted the calculations for metric cost values (Table B9).

#### 3.1 Materials and methods

#### 3.1.1 Materials

All chemicals were used as received. Fullerene mix (70% C<sub>60</sub>, 29% C<sub>70</sub>, and 1% higher fullerenes) was purchased from SES Research Group (Houston, TX), C<sub>60</sub> and C<sub>70</sub> with +99% purity from MER (Tuscan, AZ), 1,2,4-trimethylbenzene (TMB) CAS 95636 (+98%), toluene CAS 108883 (ACS reagent, +99.5%), xylenes CAS 1330207 (ACS reagent, +98.5%), linseed oil CAS 8001261 (MQ200), olive oil CAS 8001250 (MQ200, highly refined), hexane CAS 110543 (HPLC (HPLC 99.9%), grade, +85% n-Hexane), 2-propanol CAS 67630 grade, 1.8-Diazabicyclo[5.4.0]undec-7-ene (DBU) CAS 6674222 (puriss., +99% GC), 2methyltetrahydrofuran CAS 96479 (+99%), were purchased from Sigma Aldrich Burlington, MA.

# **3.1.2 Environmental impact assessment**

We used life-cycle assessment (LCA) to evaluate the environmental impacts of producing one kg of  $C_{60}$  with 99% purity. LCA was conducted using SimaPro 9.1.0.7 [169] to model  $C_{60}$ purification processes and analyze inventory data, including Ecoinvent 3.3, US-EI from DATA SMART, published articles (Table B1 in Appendix B), and data collected during experiments to quantify associated carbon footprints. We used the TRACI 2.1 V1.05 method for Global warming potential (GWP) analysis, Cumulative Energy Demand V1.11 method for energy assessment, (Water Scarcity) V1.00 method for water demand (WD) analysis [170], and E-Factor calculation [171].

#### 3.1.3 Cost and chemical hazard analysis

The cost and chemical hazard evaluation were explained in the previously published paper [104]. In summary, chemical hazard analysis was based on NFPA 704 standard scores, including health hazard, flammability hazard, reactivity hazard, and special hazard [172]. Cost assessment was based on the production rate of the target substrate and the life cycle cost (LCC) of required raw materials. These values were normalized using the values of the baseline process, then averaged into a single cost metric value for analysis.

## 3.1.4 Toxicity assessment

This study used Toxicity Estimation Software Tool (TEST, V5.1 [29]) to estimate the toxicity of petroleum-based solvents. The U.S. Environmental Protection Agency (EPA) developed TEST using Quantitative Structure-Activity Relationships (QSARs) methodologies to allow users to predict chemical toxicity based on molecular structures. We employed TEST to compare the petroleum-based solvents' toxicity based on acute toxicity (48 h) results for Daphnia Magna. The toxicity of plant-based oils was from previous work [20].

# 3.1.5 Green chemistry principles

Green chemistry principles were described in Table B2 based on Jessop et al. work [24]. This study identified alternative solvents with high  $C_{60}$  solubility (to reduce the amount of required solvents – principle #5) and lower toxicity (to reduce the risk of accidental release and avoid toxifying the final products – principle #12 & 4). We also considered plant-based solvents in accordance with principle #7, which is about using renewable feedstock.

# **3.1.6 Experiments**

The baseline process was identified by evaluating the environmental, cost, and chemical hazards of existing purification methods. In the baseline, the fullerene mix, including  $C_{60}$ ,  $C_{70}$ , and higher fullerenes, was dissolved in five mL of TMB using an ultrasonic bath for five min at room temperature [57,58]. The complexation process started by adding 103 µl of DBU and four µl of DI water in 10 min while the solution was continuously mixed at a low speed to avoid a vortex. The complexation continued for five hours under the nitrogen atmosphere to let DBU and  $C_{70}$  and higher fullerenes form a solid complex. They used a 0.2-micron filter to separate the complex containing  $C_{70}$  and higher fullerenes from the solution containing  $C_{60}$ . The remaining DBU was removed from the procedure using 0.2 M acetic acid. Isopropanol was used to separate  $C_{60}$  particles from the solution via the crystallization process in 24 h. Finally,  $C_{60}$  particles were collected for drying to remove remained solvents.

We used an iterative method [104] to modify the baseline process (Figure 3.2). The iterative approach allowed us to evaluate purification yields and apply in-process modifications. As shown in Figure 3.2, the iterative approach started with the baseline, followed by initial material characterization, screening processes based on  $C_{60}$  purity and yield, and sustainability evaluation of potential alternative procedures with a comparable purity and yield to the baseline. The best

alternative purification process was identified based on environmental, cost, and chemical hazard effects. High-performance liquid chromatography (HPLC-UV) was used to measure C<sub>60</sub> purity. The column was YMC-Pack ODS-ATM (5  $\mu$ m, 120Å, 150 × 6 mm I.D.), the mobile phase was hexane/2-propanol (70/30), the flow rate was 0.7 mL/min, the wavelength was 350 nm (0.08 AUFS), and injection was four  $\mu$ L [173].



**Figure 3.1.** The experimental approach to identify alternative  $C_{60}$  purification methods for the baseline process

# **3.2 Results**

# 3.2.1 Existing C<sub>60</sub> purification methods

Complexation with DBU was selected as the baseline process. The environmental, chemical, and cost evaluations of existing purification methods were conducted in collaboration

with colleagues. Figure B1, B2, and B3 in Appendix B present system boundary and material flow of existing commercial C<sub>60</sub> purification methods, such as complexation (Nagata, 2005), crystallization (Kwok, 2010), and crystallization (Grushko, 2007), respectively.

# **3.2.2 Baseline evaluation**

Figure 3.3 shows the environmental evaluation (CED) results of the complexation process from extracting raw materials to produce one kg of  $C_{60}$ . We could track energy consumption in the  $C_{60}$  purification process with CED to identify the associated environmental hotspots. TMB contributed to more than 95% of the total CED of the baseline purification process because of the amount of solvents and the embodied energy of TMB. It was determined as the environmental hotspot, which required a modification. Figure B1 presents the system boundary and procedure details.



Figure 3.2. Environmental evaluation of the baseline purification process (complexation with DBU)

#### **3.2.3 Alternative solvents for TMB**

TMB is a highly toxic solvent that needed to be replaced by nontoxic or less toxic solvents. We used  $C_{60}$  solubility and toxicity score to identify alternative solvents in accordance with the following green chemistry principles (Table B2 - #3: use substances with no or little toxicity, #4: design safer chemicals with lower environmental toxicity, #5: design to use less amount of solvents, #7: use renewable feedstocks, and #12: safer substrates for accident prevention). Figure 3.4 shows the toxicity scores and  $C_{60}$  solubility of available solvents. The purple area presents solvents with a lower toxicity score than TMB and comparable  $C_{60}$  solubility to TMB. Two groups of solvents were selected as potential replacements: plant-based and petroleum-based solvents. Linseed oil and olive oil were selected since they are nontoxic [174], have a higher solubility than TMB, and are extracted from renewable feedstocks. Xylene and toluene were chosen because they are also less toxic than TMB and have a comparable  $C_{60}$  solubility with TMB. The normalized toxicity score was 0.24 for TMB, 0.17 for xylene, 0.12 for toluene,  $0.12 \times 10^{-3}$  for linseed oil, and  $0.38 \times 10^{-4}$  for olive oil. The normalized solubility score was 0.34 for TMB, 0.18 for xylene, 0.16 for toluene, 1.0 for linseed oil, and 0.44 for olive oil. Table B3 presents detailed information on solvent toxicity scores and  $C_{60}$  solubility.



**Figure 3.3.** The toxicity and  $C_{60}$  solubility of solvents to identify replacements for TMB. The purple area highlights potential alternative solvents. Table B3 presents the detailed information of solvents #1 to #24.

# **3.2.4 Purification experiments**

#### 3.2.4 1 Modified baseline process

The modified baseline had lower environmental, cost, and chemical hazard impacts than the baseline. The baseline purification yield was about 44%. The low yield was originated from filtration, where we lost a considerable portion of  $C_{60}$ . A centrifuge was used to increase the production yield to 76% resulted in fewer environmental, cost, and chemical hazard impacts. The modified baseline had about 43% less chemical hazards and environmental impacts and was 22% cheaper than the baseline. We conducted experiments to reduce the environmental, cost, and chemical hazards of the modified baseline. Figure B4 demonstrates the material flow of the modified baseline.

#### 3.2.4 2 Alternative plant-based oil solvents (P<sub>1</sub> to P<sub>6</sub>)

Linseed oil and olive oil were chosen as plant-based replacements for TMB because they are less toxic, have a comparable  $C_{60}$  solubility, and are extracted from renewable feedstocks. Various methods were proposed to dissolve fullerenes in linseed oil and olive oil. In P<sub>1</sub>, fullerene was dissolved in olive oil, stirring for 72 h at room temperature under a nitrogen atmosphere, as Cataldo et al. suggested [175].  $C_{60}$  purification yield was lower than 5% because the fullerene-mix particles were not fully dissolved in olive oil at the beginning of the experiment and probably complexation only occurred at the surface. Therefore,  $C_{70}$  and higher fullerenes did not form a solid complex with DBU during the complexation. In P<sub>2</sub>, the fullerene mix was added into olive oil at 75 °C while the solution was stirred for two hours under a nitrogen atmosphere, as Cataldo et al. suggested [176]. The production yield was still lower than 5% since the oil decomposition occurred at high temperatures and reacted with  $C_{60}$ . P<sub>3</sub> was based on a suggestion to use a sonication bath for 15 min at 50 °C to dissolve fullerenes in olive oil [177–179]. The production

yield increased to 26%, much higher than  $P_1$  and  $P_2$  but still was lower than the modified baseline production yield. In  $P_4$ , we replaced the sonication bath with an ultrasonic probe to improve the amount of dissolved  $C_{60}$  in olive oil before the complexation. 100 mg of the fullerene mix was dissolved in four mL of olive oil using the ultrasonic probe for three minutes while the container remained in a water bath to keep the temperature close to room temperature. The production yield increased to 44%.

 $P_5$  and  $P_6$  were to identify the best production yield for the purification method using linseed oil instead of TMB. Linseed oil toxicity score is not less than olive oil, but its  $C_{60}$  solubility is higher than olive oil solubility, which could reduce the associated impacts to the  $C_{60}$  purification process. In  $P_5$ , we dissolved 100 mg of the fullerene mix in two mL of linseed oil using an ultrasonic bath for 15 min at 55 °C as was recommended in the literature [177–179]. The production yield was 36%.  $P_6$  was based on using the ultrasonic probe for three min at room temperature. The production yield was 61% in  $P_6$ . Figures B5 and B6 illustrate the material flow for  $P_4$  and  $P_6$ .

# 3.2.4 3 Alternative petroleum-based solvents (P7 to P8)

 $C_{60}$  purification methods using toluene and xylene had lower environmental, cost, and chemical hazard impacts than the modified baseline. Toluene and xylene were selected as petroleum-based replacements for TMB due to their high  $C_{60}$  solubility and low toxicity score compared to TMB (Figure 3.4). 100 mg of the fullerene mix was dissolved in 7.5 mL of xylene in  $P_7$  and eight mL toluene in P8. The rest of the procedures were similar to the modified baseline. The  $C_{60}$  production yield was 70% for  $P_7$  and 77% for P8. Figures B7 and B8 show the material flow for  $P_7$  and  $P_8$ . Fig B10 demonstrates the HPLC analysis of the baseline, modified baseline,  $P_4$ ,  $P_6$ ,  $P_7$ , and  $P_8$ .

# 3.2.5 Environmental, cost, and chemical hazard evaluation of potential methods

#### 3.2.5 1 Chemical hazard assessment

Chemical hazard impacts were quantified for potential alternative solvents as well as alternative purification methods. Table B4 presents the detailed calculation of solvents' chemical hazard impacts. The chemical hazard score was 1.3 for TMB, 2.0 for toluene and xylene, 0.33 for linseed oil, and 0.67 for olive oil. The chemical hazard score of alternative purification methods was calculated and normalized to the baseline (Table B5). The modified baseline chemical hazard score was 57. The highest chemical hazard score was 187, which was for the purification method using olive oil (P<sub>3</sub>). This is because olive oil regeneration requires a large amount of energy due to its high boiling point (447 K [180]); therefore, all of the olive oil used in the process was counted for chemical hazard evaluation. The chemical hazard score was 34 for the method using linseed oil (P<sub>6</sub>). It was almost six times lower than the chemical hazard score of P<sub>3</sub> since less amount of solvent was required due to the higher C<sub>60</sub> solubility of linseed oil. The chemical hazard score was even lower for the alternative methods using petroleum-based solvents mostly because toluene and xylene can be regenerated; therefore, less amount of solvents were considered for chemical hazard evaluation. The lowest chemical hazard score was 13 for the purification process using toluene instead of TMB.

#### 3.2.5 2 Cost assessment

The  $C_{60}$  purification process using toluene (P<sub>8</sub>) had the lowest cost impact. Table B6 shows the baseline and alternative purification methods' production rate. The life cycle cost was calculated based on raw materials and energy needed to produce solvents and materials used for  $C_{60}$  purification (Table B7 and B8). The processes using xylene and toluene as alternative solvents had lower cost impacts due to their low cost of production from crude oil sources (Table B9).

#### **3.2.5 3 Environmental impact assessment**

The  $C_{60}$  purification process using toluene (P<sub>8</sub>) had the lowest environmental impacts (GWP, CED, WD, and E-factor). Table B10 presents the LCA details for the baseline, modified baseline, and alternative (P<sub>3-8</sub>) purification methods. The modified baseline had about 57% less environmental impact than the baseline because of a higher purification yield than the baseline, resulting in using less materials to produce one kg of C<sub>60</sub>. C<sub>60</sub> purification with olive oil (P<sub>3</sub> and  $P_4$ ) had the highest environmental impact score. It was almost five times higher than the baseline and ten times higher than the modified baseline. Olive oil production requires a large amount of energy, water, and substrates, increasing associated environmental impacts. C<sub>60</sub> purification with linseed oil (P<sub>5</sub> and P<sub>6</sub>) had lower environmental impacts than purification with olive oil but had higher environmental impacts than the modified baseline.  $C_{60}$  purification with xylene (P<sub>7</sub>) had lower environmental impacts than purification with olive oil, linseed oil, the baseline, and the modified baseline. C<sub>60</sub> purification with toluene (P<sub>8</sub>) had the lowest environmental impacts compare to the baseline, modified baseline, and other alternative methods. Because toluene can be regenerated and reused in the process, it resulted in consuming less amount of materials necessary for C<sub>60</sub> purification. The environmental impact score of C<sub>60</sub> purification with toluene was about 60% less than the baseline and 28% less than the modified baseline.

# 3.2.6 Overall evaluation

The C<sub>60</sub> purification process using toluene was identified as a green replacement for C<sub>60</sub> purification. Figure 3.5 summarizes the evaluation of baseline, modified baseline, and alternative methods ( $P_{3-8}$ ) for C<sub>60</sub> purification based on environmental, cost, and chemical hazard impacts. Even though linseed oil and olive oil are nontoxic plant-based solvents with high C<sub>60</sub> solubility, the life cycle analysis showed that the total impacts of using them were higher than using

petroleum-based solvents (e.g., toluene and xylene). It was primarily due to the large amount of energy, water, and substrates necessary for producing olive oil and linseed oil. Also,  $C_{60}$  purification yield was low for purification methods using olive oil and linseed oil, which increased the materials necessary for making one kg of  $C_{60}$  and consequently affected associated environmental, cost, and chemical hazard impacts.



Figure 3.4. The evaluation of baseline, modified baseline, and alternative methods for  $C_{60}$  purification based on environmental, cost, and chemical hazard impacts.

# **3.3 Conclusion**

Before large-scale production, identifying a green process for  $C_{60}$  purification will reduce the environmental impacts of emerging  $C_{60}$ -containing products, such as organic transparent solar cells. Existing purification processes require a large amount of toxic solvents resulting in high environmental, cost, and chemical hazard impacts. The complexation is the best existing purification process; however, more than 95% of the environmental impact (CED) is due to using toxic TMB. Olive oil, linseed oil, xylene, and toluene were identified as potential alternative solvents for TMB since they are less toxic and have a comparable  $C_{60}$  solubility to TMB. An iterative approach was used to employ LCA and green chemistry to determine if using potential alternative solvents could result in a greener purification process.

Identifying a green solvent is highly dependent on the production process of the target product. Olive oil and linseed oil are nontoxic and have a higher  $C_{60}$  solubility than TMB, xylene, and toluene. However, the plant-based oil production process requires more energy, water, and materials than xylene and toluene in the upstream and the purification stage. Therefore, considering the life cycle of producing potential alternative solvents from raw materials and the production stage of the target product is vital for green solvent selection. It is also essential to study the chemical hazard of using potential alternative solvents. Sometimes selected solvents require extra materials to have a similar capability as the baseline solvent has. For example, olive oil is a nontoxic solvent, but a large amount of heptane, compared to what requires in the baseline, is necessary to separate  $C_{60}$  from  $C_{60}$ -containing solution results in a higher chemical hazard score.

# Acknowledgments

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# Chapter 4 Material requirement and resource availability for silicon photovoltaic laminate manufacturing in the next ten years <sup>b</sup>

Material scarcity is a considerable threat to energy transition towards renewables. Photovoltaics (PV) installations are expected to increase rapidly in the next decade, which may increase the amount of material needed. This Chapter created three scenarios ( $S_1$ ,  $S_2$ , &  $S_3$ ) to evaluate the impacts of potential technology improvements on the amount of materials necessary for manufacturing silicon PV (Si PV) laminate in the next ten years for the US and the rest of the world. The baseline was similar to previous studies, which applied theoretical models on PV historical data and ignored PV technology improvements that can influence future material projections.  $S_1$  considered only market share and module efficiency, while  $S_2$  covered wafer thickness improvements as well.  $S_3$  was the scenario that more likely will occur in the next decade, which included module efficiency, market share, wafer thickness, glass thickness, and potential replacements such as using perovskite/silicon tandem. This Chapter quantified the materials needed for Si PV laminate manufacturing in the next decade in the US and globally. We also highlighted the importance of considering technology improvements to project the PV material requirement.

# 4.1 Introduction

The global cumulative PV installation increased from one GW in 2000 to 480 GW in 2018 and is expected to reach 8,519 GW by 2050 [6][181]. PV technologies' contribution to electricity generation from renewable resources was less than one percent in 2010, while it is estimated to

<sup>&</sup>lt;sup>b</sup> Parts of this chapter were presented at the 48th IEEE -PVSC conference (June 2021).

increase from 13% in 2018 to 48% by 2050 in the USA [182]. However, the energy transition to renewable energy faces various challenges related to material availability that should be carefully explored [183].

Material scarcity is a potential threat to PV deployment. In 2019, silicon PV (Si PV) was 95% of the PV market [6]. Si PV is anticipated to remain the primary type of PV technology (>50%) until 2040 [22]. Most previous studies on the material need for Si PV used theoretical models such as material flow analysis [184], the total material requirement [185], Hubbert peak [8][9], and historical data to project future material necessary for manufacturing Si PV in the future need. A few studies considered market share and efficiency changes while ignoring changes in technology and manufacturing [188–190].

In this Chapter, we calculated the materials such as metallurgical grade silicon (MG-Si), solar glass, aluminum, copper, lead, silver, and tin needed for manufacturing Si PV laminate to meet the expected annual Si PV installation in the next ten years for the US and rest of the world. We considered module efficiency, the percentage of Si PV sub-technologies in the PV market, silicon wafer thickness in cells, glass thickness in laminate, sawing techniques, and other potential technology improvements such as using silicon/perovskite tandem.

# 4.2 Methods

#### 4.2.1 Study scope

This study considered materials necessary for manufacturing Si PV laminate. Figure 4.1 shows the study scope, which contains mining raw materials, solar-grade material production, wafering, cell processing, and PV laminate manufacturing. MG-Si is required for producing solar-

grade silicon. Silver and aluminum are needed for metallization paste at the cell production stage. Copper, tin, lead, and solar glass are considered for PV laminate.



Figure 4.1. The study scope to quantify materials needed for manufacturing Si PV laminate.

# 4.2.2 Material requirement

Materials necessary to support Si PV were calculated based on data compiled from literature, energy outlooks, and the annual reports of leading Si PV manufacturers. The annual PV installation was based on the 2020 DNV-GL Energy Transition Outlook (Figure C1 in Appendix C) [13]. PV technology improvements, such as efficiency, wafer thickness, wafer sawing, glass thickness, and material replacement, were determined based on leading manufactures' annual reports and energy outlooks. I identified the required materials for the baseline and three scenarios  $(S_1, S_2, \& S_3)$  for the USA and the rest of the world (Table 4.1). The baseline assumptions were similar to previous PV studies that used theoretical models and PV historical data to calculate the necessary materials for PV manufacturing and ignored technology changes. S<sub>1</sub> and S<sub>2</sub> were similar to previous studies where some part of technology improvement was considered to estimate materials required for making PV. S<sub>3</sub> considered Si PV sub-technologies' efficiency and contribution to the PV market, silicon wafer thickness, glass thickness, sawing techniques, and perovskite/silicon tandem.

Scenario	Description							
Baseline	Efficiency, market share, and	emain constant u	ntil 2031					
	· · · · · · · · · · · · · · · · · · ·			2021	2031			
	Sub-technology Market	c-Si*	35.5 [3]	28.22 [191]				
G	share (%)		mc-Si**	64.5 [3]	40.61 [191]			
51	Efficiency (%)	c-Si		22 [3]	23.5 [191]			
			mc-Si	19 [3]	22 [191]			
	Sub-technology Market	c-Si		35.5 [3]	28.22 [191]			
	share (%)	mc-Si		64.5 [3]	40.61 [191]			
S.	Efficiency (%)		c-Si	22 [3]	23.5 [191]			
52		mc-Si		19 [3]	22 [191]			
	Silicon wafer thickness	c-Si		170 [4]	50 [39]			
	(μm)	mc-Si		180 [4]	50 [39]			
			Al-BSF	3.44	0			
		c-Si	Monofacial PERC	14.58	5.82			
			Bifacial PERC	14	20.64			
			Monofacial HJT	1.05	1.45			
			Bifacial HJT	1.01	5.16			
	Sub-technology Market		Bifacial	0.97 (2023)				
	share in PV [39]		perovskite PERC		5.18			
		mc-Si	Al-BSF	6.35	0			
~			Monofacial PERC	26.89	5.8			
<b>S</b> <sub>3</sub>			Bifacial PERC	25.84	20.64			
			Monofacial HJT	1.94	1.45			
			Bifacial HJT	1.87	5.16			
		Al-BSF c-Si		20	21.5			
		Al-BSF mc-Si		19	20			
	Efficiency	PERC c-Si		20.7	22.2			
	[39]	PERC mc-Si		19.5	21.5			
		HJT Si		21.5	23			
		Si/perovskite tandem		22.5	26			
	Silicon wafer thickness	c-Si		170 [4]	50 [39]			
	(µm)	mc-Si		180 [4]	50 [39]			
	Glass thickness (mm) [39] c-Si & mc-Si		4	2				

Table 4.1. Assumptions for each scenario to project materials needed for Si PV manufacturing

\*mono-crystalline silicon (c-Si), \*\*multi-crystalline silicon (mc-Si)

We used a bottom-up approach to determine the required materials for manufacturing Si PV laminate (Appendix C2). Figure 4.2 shows the six types of Si-based solar cells considered: aluminum back surface field (Al-BSF), mono facial PERC, bifacial PERC, mono facial Si heterojunction (HJT), bifacial HJT, and perovskite/silicon tandem.



**Figure 4.2.** The typical structures of Si PV. Al-BSF: Aluminum Back Surface Field, PERC: Passivated Emitter and Rear Cell, HJT: Heterojunction Technology. [192–196]

# 4.2.3 Resource availability

Material availability for Si PV manufacturing was based on the United Nations Comtrade annual reports [197] and the United States Geological Survey Minerals Yearbooks [198]. Annual MG-Si and silica sand production were identified using yearly USGS reports [199].

# 4.3 Results and discussion

# **4.3.1 Material requirements**

We estimated the amount of required materials for manufacturing Si PV laminate based on a linear regression between 2021 and 2031. Wafer thickness for Si PV was assumed to be 180  $\mu$ m for mc-Si and 170  $\mu$ m for c-Si in 2020 [4] and reduced to 50  $\mu$ m by 2031 [200]. The 2021 market share for c-Si and mc-Si PV was 35.5 % and 64.5%, respectively [201]. The Si PV market share is expected to shrink to 25% for c-Si and mc-Si PV by 2040 [191]. Cadmium telluride (CdTe), copper indium gallium selenide (CIGS/CIS), and silicon tandem with perovskites are expected to cover the rest of the PV market. The efficiency was assumed to improve from 22% (c-Si PV) and 19% (mc-Si PV) [3] to 25% in 2040 [191]. However, this was higher than the Si PV efficiency reported for mass production. For example, the median efficiency of Al-BSF c-Si produced by leading global PV manufacturers is about 20% in 2021 and may reach 21.5% by 2031 [200]. In the  $3^{rd}$  scenario (S<sub>3</sub> – Table 4.1), we considered market share changes and efficiency improvements for each Si PV sub technology for mass production; Al-BSF, mono facial PERC, bifacial PERC, mono facial HJT, bifacial HJT, and perovskite/silicon (Figure 4.2).

Figure 4.3 shows the material required for manufacturing Si PV laminate to meet the global PV installation forecasts until 2031. Solar glass and MG-Si will have the highest demand in the next ten years. The baseline shows how material demands are increasing due to the increase in PV installation without considering any changes in PV technology. In the next decade, material demand will increase by 260% for MG-Si and 250% for solar glass (Figure 4.3A). The first scenario (S<sub>1</sub> - Figure 4.3B) shows how efficiency improvements and market share changes may influence material needs in the next couple of years. For example, in 2031, about 1.04 million metric tons of MG-Si and 13.1 million metric tons of solar glass will be required for the baseline, while it is 0.69 million metric tons of MG-Si and 9.3 million metric tons of solar glass for S<sub>1</sub>. For the second scenario (S<sub>2</sub> – Figure 4.3C), we considered the reduction in wafer thickness. For S<sub>2</sub>, the amount of MG-Si was 69% lower than S<sub>1</sub>.

The 3<sup>rd</sup> scenario (Figure 4.3D) was based on data collected from mass production in global leading PV manufacturers. Similar to the baseline, S<sub>1</sub>, and S<sub>2</sub>, MG-Si and solar glass were the primary materials for making Si PV laminate. However, the material demand in 2021 was higher due to the low efficiency of massive Si PV production compared to the Si PV efficiency reported by previous studies. Manufacturing improvements such as the decrease in the thickness of Si wafer and glass as well as using emerging technologies such as perovskite will mitigate material demand.

The material demand is expected to be reduced after 2029 due to the possibility of replacing Al-BSF with other Si PV with higher efficiency.



**Figure 4.3.** Material requirements for manufacturing Si PV to meet the electricity demands from 2021 to 2031 for various scenarios globally. (A) Baseline , (B)  $S_1$ , (C)  $S_2$ , and (D)  $S_3$ . Material requirements for the US and the rest of the world are shown in C2 and C3.

Figure 4.4 shows material requirements for manufacturing Si PV laminate for subtechnologies in the 3<sup>rd</sup> scenario. MG-Si and solar glass were the primary materials for each subtechnology. Required MG-Si for Al-BSF Si PV (Figure 4.4B) will decrease from 43,000 metric tons in 2021 to 3,000 metric tons in 2030 due to replacing Al-BSF Si PV with other Si PV technologies. The solar glass will also decrease from 585,000 metric tons in 2021 to 71,000 metric tons in 2031

PERC Si PV (Figure 4.4B) will need the highest amount of materials among Si PV technologies. PERC technology was 83% of the Si PV market and is expected to shrink to 72% in 2031 [200]. About 346,000 metric tons of MG-Si and 6.1 million metric tons of solar glass were needed in 2021 for manufacturing PERC Si PV laminate which will decrease to 177,000 metric

tons of MG-Si and 5.3 million tons of solar glass. HJT Si PV (Figure 4.4C) was 6% of the Si PV market in 2021 and is likely to be 18% of the Si PV market in 2031 [200]. MG-Si demand will increase from 30,000 metric tons in 2021 to about 55,000 metric tons in 2031. A similar trend was projected for solar glass, where the demand increased from 0.56 million metric tons in 2021 to 1.78 million metric tons in 2031. The last technology in the Si PV market is perovskite/silicon tandem which is expected to be a part of mass production after 2023 [200]. MG-Si demand for manufacturing perovskite/silicon tandem will increase about 2.5 times in the next couple of years. Approximately 4,000 and 14,000 metric tons of MG-Si will be required in 2023 and 2031, respectively.



**Figure 4.4.** Material requirements for manufacturing Si PV technologies to meet the electricity demands from 2021 to 2031 globally. (A) Al-BSF Si PV, (B) PERC Si PV, (C) HJT Si PV, and (D) Si/Perovskite tandem. Material requirements for the US and the rest of the world are presented in C4-C11

#### 4.3.2 Resource availability

Figure 4.5 shows available silica sand and MG-Si resources in 2020. Industrial-grade silica sand is the primary material for producing solar glass and MG-Si. Some countries such as the US,

the Netherlands, and Spain had the highest amount of available silica sand resources in 2020 (Figure 4.5A). MG-Si is the other key material for the Si PV market, which is mainly produced in China. Other leading MG-Si producers were Russia, Norway, and the US in 2020 (Figure 4.5B). The primary stockpiles' users are the aluminum and chemical industry for MG-Si and the concrete, roads, and construction industry for silica sand. In contrast, the PV industry consumed a small percentage of MG-Si and silica sand [199]. However, PV deployment growth may increase the dependency of Si PV producers on MG-Si and high-quality silica sand resources. This may result in competition between various stakeholders to supply material demand for Si PV manufacturing which may affect the environment due to the possibility of excessive mining or using illegal silica sand.



Figure 4.5. Available industrial-grade silica sand (A) and MG-Si (B) in 2020.

# 4.3.3 Conclusion

The material shortage is a potential issue for PV deployment. This Chapter showed the importance of considering PV technology improvements in material projections. We evaluated Si PV material demand for different scenarios to cover typical assumptions considered by previous studies for material requirement estimations. The baseline was representative of previous studies
that conducted analysis only based on historical data and ignored PV technology changes. The first and second scenarios were based on assumptions used by previous studies, where they focused only on efficiency and market share and ignored sub-technology deployment and manufacturing improvements. In the 3<sup>rd</sup> scenario, we projected material requirements considering improvements in the efficiency and market share of c- and mc-Si PV sub-technologies, glass thickness, and Si wafer thickness in the next decade. The estimated required materials in S<sub>3</sub> were 22% to 78% lower than the baseline and 23% to 66% lower than 1<sup>st</sup> and 2<sup>nd</sup> scenarios. MG-Si and solar glass have the highest demand for Si PV laminate manufacturing. About 74 billion metric tons of solar glass and 3 billion metric tons of metallurgical grade silicon will be required in the next decade for Si PV laminate manufacturing.

The availability of silica sand resources for MG-Si and solar glass production may cause some challenges for Si PV producers, which could result in excessive mining that may increase the socioenvironmental impacts of Si PV. There is also a possibility of using silica sand from illegal mines due to accessibility to enough resources. It is essential to consider third-party certifications to monitor the Si PV supply chain to ensure Si PV materials will be provided from legal mines without severe impacts on the environment.

## Acknowledgment

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# Chapter 5 The country-specific footprint of metallurgical grade silicon production for silicon photovoltaics

The carbon footprint of quartz mining and silica sand extraction is widely ignored in photovoltaic (PV) studies. The PV industry requires high-quality silica sand to produce metallurgical grade silicon (MG-Si) used to manufacture silicon PV (Si PV). However, high-quality deposits are scarce, and using lower-quality resources may increase the carbon footprint of Si PV modules. This Chapter quantified the current and future carbon footprint and cumulative energy demand (CED) of quartz mining, silica sand extraction, and MG-Si production. The life-cycle assessment was used to evaluate the carbon footprint of producing one kg of MG-Si using quartz deposits with different purity levels: high-quality (> 98% silica), industrial-grade (95% silica), and low-quality (65% silica).

# 5.1 Background

Photovoltaics (PV) is a promising energy technology to reduce the carbon footprint of electricity production [202]. Cumulative PV installations have increased from one GW in 2000 to 480 GW in 2018 and will reach 8,519 GW by 2050 [6]. Silicon PV (Si PV) represents 97% of the current PV market and is expected to remain the dominant technology until 2040, but raw material shortage could reduce the market share of Si PV [203]. The raw material for Si PV is quartz which is mined to extract silica sand and purified to produce metallurgical grade silicon (MG-Si) [4] (Figure 5.1). Further purification is necessary to remove impurities such as Fe, Al, B, and P to produce solar-grade silicon [204] used in photovoltaic cells.



**Figure 5.1.** Study scope including quartz mining, silica sand extraction, and MG-Si production for manufacturing Si PV modules

Life-cycle assessment (LCA) is widely used to evaluate the carbon footprint of Si PV. The quartz purity and availability were not considered in previous Si PV LCA studies. Figures (D1-D4) in Appendix D summarize Si PV LCA studies from 2000 to 2019. Previous work either focused on the carbon footprint of processes after producing MG-Si or ignored the extra steps necessary for extracting high-quality silica sand from low-quality and industrial-grade quartz resources to make MG-Si. Latter studies used the mining processes of a sand producer in Germany and only added a drying step to model high-quality silica sand extraction (Table D1 in Appendix D). This assumption is valid only if the quartz contains more than 98% of silica. However, only a few places in the world have quartz deposits with that level of purity. The rest of the available quartz resources are industrial (95% purity) or low-quality grade, which need more steps than high-quality quartz to remove impurities from quartz and extract silica sand.

Industrial-grade silica sand extraction was modeled in a few studies but not the extraction and purification of low-quality silica sand. The carbon footprint of extracting industrial-grade silica sand for glass in Croatia was calculated to be 43 kg  $CO_{2eq}$  per metric ton of silica sand [205]. In another study, the impact of 99% purity silica sand extraction for foundry application in Poland was calculated for natural resource consumption, ecosystem quality, and human health but not the carbon footprint [206]. According to annual reports from high-quality silica sand producers such as Unimin Corporation [207], extra processes are necessary to separate impurities from quartz. Those extra processes require a large amount of fossil fuels; therefore, mining lower quality quartz may increase the carbon footprint of Si PV.

In addition to the environmental impacts, there are potential social issues associated with quartz mining for Si PV manufacturing [208]. Current environmental regulations do not consider social impacts associated with mining [209,210]. Multiple frameworks have been suggested to investigate the social impact of the mining industry but not for silicon. Quartz mining undermines local livelihoods and has been identified as the world's most conflict commodity [211]. Silica sand extraction is growing, generating serious social concerns in India [211], China [212], and the USA [213]. In the USA, Wisconsin is the main industrial-grade silica sand provider for the hydraulic fracturing industry. Multiple reports from anti-fracking activists show that some people lose their land, others suffer from the destruction of the natural system, and all are exposed to new environmental health risks [213]. Some solutions, such as combining environmental cost estimation and using developed efficient extraction plans, may reduce the conflicts among silica sand producers and local residents [214,215]. All existing studies consider only legal mines and ignore the social impacts of extracting raw materials such as silica sand from illegal mines, likely due to the lack of information such as the mine's location. The United Nations Environmental Program also started investigating quartz mining activities in 2018 but faced many obstacles due to the lack of information on the location of quartz deposits and their legality [216,217].

The increase in PV installations will increase the demand for silica sand. This Chapter evaluated the carbon footprint of silica sand extraction from various purity and location to meet the demand for Si PV manufacturing. We compiled the availability and the purity of quartz deposits in the USA, China, and the rest of the world for producing Si PV in the present and future. The main MG-Si producers in China and the rest of the world were identified. The amount of silica sand and MG-Si production were compiled for Africa, America, Asia and Pacific, China, and Europe. We modeled quartz mining, silica sand extraction, and MG-Si production processes for the high-quality (>98% purity), industrial-grade (95% purity), and low-quality (65% purity) deposits to quantify the associated carbon footprint. Global warming potential (GWP) and cumulative energy demand (CED) were calculated for various scenarios to estimate the environmental impacts of silica sand extraction and MG-Si production at present and in the future. This Chapter also identified the location of illegal mines that MG-Si producers might use.

#### 5.2 Methods

The first step was to collect data on the location of quartz deposits and purification, the annual silica sand production per country, and the annual import/export amount of silica sand between leading producers and primary consumers. In the second part, we used life-cycle assessment to calculate the carbon footprint associated with quartz mining, silica sand extraction, and MG-Si production needed to manufacture Si PV.

## 5.2.1 Location of legal and illegal mines and MG-Si production

Data about the location, purity, annual production of active legal mines in the USA, China, and other countries was collected from the 2020 U.S. Geological Survey (USGS) report [199], United Nations Comtrade Database (UN Comtrade) [197], companies' annual report (Diatreme Resources Ltd [218] and Unimin (COVIA) Corporation [207]), and literature [216,219–239]. Data about the location of illegal mines was obtained from articles published in local and international news agencies from 2017 to 2020 [240–249], NGO reports [250,251], and published papers [252–254]. The annual production and location of MG-Si producers were compiled from 2020 USGS reports [199,255].

### 5.2.2 Environmental impact assessments

#### 5.2.2 1 Life cycle assessment (LCA)

The objective of the LCA was to evaluate the carbon footprint of 1 kg of >99% purity MG-Si for Si-PV. The stages within the system boundaries were quartz mining, silica sand extraction, and MG-Si production (Figure 5.1). The life cycle inventories for this study were taken from published papers (Table D2), the International Energy Agency (IEA) PVPS Task 12 [4], Ecoinvent 3.6 Database [256], and DATA SMART LCI (US-EI 2.2) [257]. Life cycle impact assessment was conducted using SimaPro [169]. ReCipe2016 method was used for global warming potential (GWP) analysis, and Cumulative Energy Demand V1.1 was used for the energy assessment. The IEA PVPS recommends GWP and CED metrics to evaluate the environmental impact of photovoltaics [4].

### 5.2.2 2 Quartz mining, silica sand extraction, and MG-Si production

The process for silica sand extraction from high-quality (>98%), industrial-grade (95%), and low-quality (65%) quartz deposits were based on existing industrial processes. The Unimin Co process was selected to model the silica sand extraction process since they are the leading global silica sand producer and transform quartz of various purity. We divided the silica sand extraction into two main steps (Figure 5.2) [207]. The first step (quartz mining) begins with removing the topsoil with loaders and bulldozers, excavating with excavators, transporting with lorry and conveyor belts, sieving, washing, and dewatering. This step is similar for high-quality, industrial-grade, and low-quality deposits. The second step (silica sand extraction) depends on quartz purity and includes beneficiation processes such as magnetic separation, flotation, and gravity separation to remove impurities physically or chemically. There is no need to use the

beneficiation process for mines with the highest purity except for drying silica sand before transportation to MG-Si facilities. In contrast, in mines with industrial-grade and lower quality, beneficiation processes are required to remove impurities.

Input data for the LCA, including required electricity and fuel at each stage, was estimated based on existing similar processes in literature (Table D2). We used the USA average electricity mix for the USA because quartz deposits are distributed all around the country. The regional electricity was selected for China since potential quartz deposits are distributed in some regions, primarily east and southeast. A significant regional difference was reported for electricity in China [258]. China's electricity was divided into six regions (Northwest, North, Northeast, East, South, and Center) based on energy resources for electricity in earlier research [258]. We selected a representative province for each region based on the highest demand for silica sand. For example, Xinjiang had the highest demand for silica sand and was chosen as a Northwest region representative. Beijing, Liaoning, Fujian, Yunnan, and Sichuan were selected for North, Northeast, East, South, and Center, respectively.



**Figure 5.2.** The process of quartz mining and silica sand extraction. The 1<sup>st</sup> step is similar for all types of quartz. The 2<sup>nd</sup> step depends on quartz purity. \*Silica sand purity depends on initial quartz quality, mining process, and extraction chosen.

Purification is required to increase the purity of silica sand to produce MG-Si with more than 99% purity. At this stage, purified silica sand is called MG-Si. Further purification is necessary to provide solar grade silicon with 99.99999% purity that can be used for Si PV module manufacturing. We modeled only MG-Si production for this study since the silica sand quality does not affect the rest of the manufacturing processes if the produced MG-Si reaches more than 99% purity. The MG-Si production process was modeled based on IEA PVPS Task 12 and Ecoinvent (Table D2).

# 5.3 Results and discussion

## 5.3.1 Location of legal and illegal quartz mines and MG-Si production

## 5.3.1 1 Legal mines

The annual production of industrial-grade silica sand per continent was compiled from 1994 to 2019 (Figure 5.3). The global production in 2019 was 329 million metric tons, with 35%

of the production in North America, 46% in Europe, and 12% in the Asia-Pacific region (APAC). The USA was the main industrial-grade silica sand producer, and 73% of its annual production was used for hydraulic fracturing [199]. The Netherlands produced 37% and Spain 24% of the European production. In APAC, India (30%) and Malaysia (25%) were the leading producers.



**Figure 5.3.** Annual industrial-grade silica sand production in the world from 1994 to 2019. Data was compiled from USGS annual reports [199].

Figure 5.4 shows the mine's locations of the USA's top ten high-quality and industrialgrade silica sand producers. Most US quartz mines are located in Illinois, Ohio, Michigan, Texas, and North Carolina Unimin Corporation is the largest producer with an annual capacity production of more than 41 million metric tons and 21 active quartz deposits in the USA [207,233,259]. US Silica Inc. is the second-largest silica sand producer in the USA, with an annual production of 19 million metric tons and 15 mines [199,260].



Figure 5.4. The mines distribution of 10 major high-quality and industrial-grade silica sand producers in the USA

High-quality silica sand is scarce, and only a few high-quality deposits, such as the Spruce Pine in North Carolina, USA, exist in the world [233,261]. The location and amount of global industrial-grade quartz deposits in 2019 were compiled (Figure 5.5A). Although typical sand is found everywhere, high-quality and industrial-grade silica sand resources are not equally distributed, and some countries suffer from a high-quality deposits' shortage. In contrast, China has no domestic high-quality and industrial-grade deposits and is highly dependent on silica sand imports [234,250] (Figure 5.5B). The main silica sand suppliers for China MG-Si production have shifted from the USA and Vietnam until 2012 to Cambodia, Australia, Malaysia, and Pakistan. Other countries like India and the United Arab Emirates also do not have enough high-quality resources to meet their growing demand. As reported by the UN, a portion of this global demand was supplied via documented international trades between producers and consumers,.



**Figure 5.5.** (A) Global distribution of industrial-grade quartz (95% SiO<sub>2</sub>) mines in 2019. Data was collected from USGS annual reports [199]. (B) Annual industrial-grade silica sand export to China. Data was compiled from the annual UN Comtrade reports [197]

# 5.3.1 2 Illegal mines

Quartz is the second most illegally traded product [262]. A review of news articles and NGO's reports was conducted to identify illegal quartz mines worldwide. Countries such as China, India, and Singapore with high growth rates need a large amount of silica sand to expand their high-tech industries, such as Si PV [254]. This demand has increased silica sand prices, which makes illegal trades more attractive. For example, Singapore's silica sand price has increased from 3 to190 \$/metric ton in the last ten years [216]. Illegal sand trades were also reported in various locations in India (Figure D13) [245–247,263–266]. In Kerala alone, in 2017, sand valued at 2.3 billion USD on the black market was removed from local rivers at a rate 40 times faster than nature can recover [226,251,265]. Mumbai city is another example of an area with high illegal trade. In 2016, more than 30,000 instances of illegal sand trading were reported. [226]. Illegal sand trades were also reported in other parts of the world, Tanzania, Kenya, Morocco, South Africa, and Sierra Leon in Africa and Colombia in South America [216,267]. Morocco supplied half of the silica sand demand (10 million metric tons per year) from illegal quartz mining [216].

Many illegal mining activities were reported in countries close to China. To produce one kg of MG-Si (>99% purity), 2.7 kg of industrial-grade quartz (95% purity) is required [4]. In 2019, China needed to import 12.15 million metric tons of industrial-grade silica sand from foreign resources for MG-Si production. However, only 14% of this amount can be accounted through documented trades. Meanwhile, multiple reports from NGOs and news agencies have identified illegal mining in Cambodia and North Korea that supply silica sand to China. (Figure 5.6) [220,242,251]. Knowingly or not, some Chinese MG-Si producers might have used silica from those illegal mines.



**Figure 5.6.** Illegal silica sand mines along the Mekong River in Cambodia and within Haeju Bay in North Korea.

## 5.3.1 3 MG-Si producers

The location of MG-Si producers (Figure 5.7A) and the amount of annual MG-Si production (Figure 5.7B) were compiled. Since 2005, the global MG-Si production has increased by about 60%, and in 2019, China, Russia, Norway, and the USA were the main producers. China

produced 64% of the global MG-Si production in 2019. Yunnan, Xinjiang, Sichuan, Guizhou, Hunan, and Fujian province produced more than 85% of 2019 MG-Si production in China.



**Figure 5.7.** (A) The global distribution of MG-Si production. (B) annual MG-Si production from 2005 to 2019 (adapted from [199])

#### **5.3.2** Environmental impact assessments

#### 5.3.2 1 Modeling silica sand extraction

Silica sand extraction from low-quality quartz needs extra beneficiation steps to remove impurities. The beneficiation processes were selected based on the types and locations of mines. For mines with access to natural water resources like rivers, the gravity method is appropriate since it requires large amount of water. However, residual sediments might affect the downstream river ecosystem. The high purity quartz resources in China are shown in Figure 5.8. They are mostly located in Chaina's east, south, and center and have an average purity of 65% [234,235]. Figure 5.8 also shows available foreign silica sand resources for China. We modeled quartz mining and silica sand extraction process for various scenarios to evaluate the carbon footprint of supplying silica sand needed for MG-Si production in China now and in the future. Table 5.1 describes the scenarios considered.



**Figure 5.8.** (A) The regional production of MG-Si (colored provinces) (adopted from [199,268]), potential domestic quartz deposits (colored dots), and foreign available silica sand resources (colored hexagonal) for China. For foreign resources, legal and illegal trades are in green and red, respectively. (B) Regional electricity for China was compiled based on the previous study [269]

LCA Scenario	Description
Baseline	Extracting silica sand from High-quality deposits (>98% purity)
Extracting silica sand	low-quality quartz using the gravity separation technique
from domestic	low-quality quartz using the flotation technique
sources	low-quality quartz using the magnetic separation technique
Imported industrial-	Australia (AU)
grade silica sand from	Cambodia (KH)
•••	Malaysia (MY)
	Pakistan (PK)
	51% AU, 45% KH, 1% MY, and 3% PK

Table 5.1. LCA scenarios for quantifying the carbon footprint of supplying silica sand for China

The GWP and CED of extracting silica sand from high-quality (>98% silica) and industrialgrade quartz (95% silica) were calculated for the USA (Figure 5.9A and D). The average GWP of extracting one metric ton of silica sand from high-quality deposits in the US was 22.7 kg of  $CO_{2eq}$ , while it was almost double (47.9 kg of  $CO_{2eq}$ ) for industrial-grade deposits due to the beneficiation processes needed to remove impurities from industrial-grade quartz. A similar trend was observed for CED. The required energy for extracting silica sand from high-quality deposits was 339 MJ/metric ton of silica sand, and it increased to 1,010 MJ for industrial-grade quartz. Figure 5.9B and C present the GWP of silica sand for MG-Si production in China. The baseline scenario for China was based on high-quality quartz. The GWP of imported industrialgrade silica sand from legal mines in Australia, Pakistan, Malaysia, and Cambodia was 117, 78.3, 69.3, and 58.3 kg CO<sub>2eq</sub>, respectively (Figure 5.9B). For illegal mines in North Korea, the GWP was 46.8 kg CO<sub>2eq</sub>. The difference by country is due to differences in electricity mix and fuel types necessary for mining operations and distance to China. When considering silica sand imports reported by the UN (51% Australia, 45%, Cambodia, 1% Malaysia, and 3% Pakistan), the GWP was 88.9 kg CO<sub>2eq</sub>. For domestic low-quality quartz, the GWP was 74.6 to 86.7 kg CO<sub>2eq</sub> per metric ton of silica sand, depending on the type of beneficiation processes (Figure 5.9C). The flotation technique had a higher GWP compared to other techniques since it requires more fuel for operations.

The lowest CED was for importing industrial silica sand from illegal mines in North Korea, which was 875 MJ per metric ton of industrial silica sand (Figure 5.9E). The highest CED was 1,890 MJ for Australia. The CED of domestic low-quality quartz was 1,120 to 1,580 MJ (Figure 5.9F). This value was 16-40% lower than importing industrial silica sand from Australia but 28-81% higher than importing silica sand from North Korea and 8-52% from Cambodia. CED is an indicator of product cost [270]. Therefore, importing industrial-grade silica sand from Cambodia and North Korea would be cheaper than using domestic low-quality resources or importing from Australia, Pakistan, and Malaysia.

One way of reducing the use of illegal quartz for Si manufacturing would be through PV supply chain tracking and certification by a third party. The transition from fossil fuels to renewable energy resources such as PV has remarkable benefits to society and the environment. However, the possibility of unlawful activities such as using illegal quartz in the PV supply chain

may threaten the original benefits of using PV. The PV consumers desire to purchase ethical PV products, while recent news agencies have reported some illegal activities in PV supply chains. Therefore, it is essential to monitor supplying quartz for the Si PV industry to ensure illegal mining is not used for PV production. In this regard, the Green Electronics Council (GEC) has recently started working with NSF International, the public health and safety organization, to develop standards for sustainable PV modules [271]. GEC has also introduced ecolabel as an easy way that manufacturers can differentiate their products from others and ensure consumers that the products meet sustainability criteria. In another effort in February 2021, the Solar Energy Industries Association (SEIA) and about 175 solar companies have signed an agreement opposing using forced workers in PV supply chains [272]. Similar types of criteria and agreements are vital to mitigate the destructive footprints of using illegal quartz in the PV supply chain.

We identified social concerns due to illegal mining based on a literature survey of news articles from the last five years. Quartz mining is becoming a global socio-environmental challenge. The mining industry may positively impact local communities' development by creating direct and indirect jobs. However, the possibility of excessive excavation in illegal mining may have adverse effects in the long term, even though there might be short-term financial benefits for local communities. Mining silica sand from oceans and riverbeds is more interesting since they are naturally crushed and ready to use. Riverbank sand is cheaper since there is no need to remove the salt [217]. But illegal and excessive mining in rivers and oceans could create severe social and environmental problems.

In Indonesia, 24 small islands and their ecosystems disappeared between 2005 and 2010 due to excessive quartz mining and silica sand extraction to export to Singapore [240]. The Mekong River is another example that silica sand mining threatens the ecosystem. The Mekong River is the 10th longest river globally and starts from China and passes through Laos, Thailand, Vietnam, and Cambodia. The largest extractors are located in Cambodia, where they extract 33 million metric tons of silica sand per year [220]. Excessive silica sand mining may change the river morphology and erosion pattern, affecting fisheries and, consequently, threatens the main food source of 60 million people living in that region, as is stated in the literature [226,228]. Farmers' incomes can also be affected due to excessive mining activities. A 20% reduction in Cambodia was reported due to a lack of agricultural lands [231].

Quartz mining may also affect communities' livelihood. In a survey study in a village in Tangail District in Bangladesh, the local community was concern about potential disasters and the black market due to quartz mining activities near their livelihoods [273]. Depletion of groundwater, reduction of soil ability to provide nutrients, increase the pH water and turbidity of the river, destruction of infrastructures, riverbank collapse, and social collapse are only some examples of mining silica sand in rivers that are also reported in the literature for mining activities [216,222,226,274–276]. Those socio-environmental impacts can be more severe for illegal mines due to a lack of legislation and public awareness.

Recent changes in legislation in Cambodia have limited silica sand extraction in the Mekong River and may affect export to China, which could affect Si PV manufacturing. However, it is reported that China has already started developing new low-cost purification methods [234,235,250] and will likely start using domestic low-quality quartz resources.



**Figure 5.9.** The GWP (A, B, C) and CED (D, E, F) of silica sand production for MG-Si production in the US and China

### 5.3.2 2 Producing MG-Si from silica sand in the USA and China

The quartz purity affects the carbon footprint of producing MG-Si in China. The GWP to produce one kg of MG-Si from imported industrial-grade silica sand was 12.1 kg CO<sub>2eq</sub> (Figure 5.10A). In comparison, using domestic low-quality quartz produced 16.5 kg CO<sub>2eq</sub>, which is a 36% increase compared to imported industrial-grade silica sand. The GWP of producing one kg of MG-Si in the USA was 12.0 kg CO<sub>2eq</sub>. Quartz purity also influenced the amount of required energy for producing MG-Si. The CED of producing one kg of MG-Si from current resources (imported industrial-grade silica sand from 51% AU, 45% KH, 1% MY, and 3% PK) was 188 MJ and increased by 53% (286 MJ) if domestic low-quality quartz resources were used instead (Figure 5.10B). Silica sand purification requires a large amount of energy due to the required high temperature (about 1,800 °C) to remove impurities from silica sand. Low-quality quartz contains more impurities and consequently requires more energy. The CED was 186 MJ for producing one kg of MG-Si in the USA.



Figure 5.10. (A) The GWP and (B) CED of producing MG-Si from high- and low-quality silica sand.

The carbon footprint of MG-Si depends on the quality of quartz. Previous LCA Si PV studies did not evaluate the carbon footprint of MG-Si production based on the location due to a lack of information for silica sand production [277]. They reported MG-Si carbon footprint based on using high-quality quartz. However, as this study showed, high-quality quartz deposits are rare, and probably most of the MG-Si companies use lower quality quartz which can increase the associated carbon footprint.

# **5.4 Conclusion**

Manufacturing Si PV requires large amounts of raw materials, including quartz. Quartz purity affects the carbon footprint of producing MG-Si used in Si PV. Previous studies focused only on scarce material and ignored quartz, probably since quartz deposits are perceived as abundant and available everywhere. Some countries, such as China, the global leading Si PV producer, do not have high-quality (>98% purity) and industrial-grade (95% purity) quartz deposits and are highly dependent on foreign resources. Regulations restricting silica sand export to China

may force Chinese MG-Si producers to use domestic low-quality (65% purity) quartz. China produced about 4.5 million metric tons MG-Si (64% of global production) in 2019 (Figure 5.7). The transition from importing high-quality or industrial-grade silica sand to mine low-quality domestic quartz can increase MG-Si production's annual carbon footprint by at least 23% (Figure 5.10). This corresponds to the annual greenhouse gas emissions from about nine million passenger cars. Si PV companies should improve the efficiency of existing MG-Si production before using low-quality quartz resources and increasing the carbon footprint of PV. Upgraded MG-Si is a new technology that can be a replacement for existing MG-Si production processes in terms of cost and carbon footprint [277]. Other sources of silica should be considered for MG-Si production, including secondary resources such as rice husk ash [278] and gold mining tails to reduce the pressure on natural resources [279].

In addition to the environmental impact of MG-Si production, the social impacts associated with quartz mining are not often discussed in the literature. Global silica sand production has tripled in the last decade. Even though the implication of quartz mining projects can have short positive effects such as creating temporary jobs for locals, it may have severe long impacts on local livelihood, particularly in regions with limited regulations. The New York Times has recently reported that some countries have regulations that may let MG-Si producers hire forced workers from ethnic minorities in an unacceptable condition [212]. Apart from inefficient rules for quartz mining, illegal mines can have more severe impacts on the environment and local communities, which are also ignored in the literature. Solar PV is a greener alternative to current electricity production, but its image could be tarnished by an increasing manufacturing carbon footprint, or even worst, using quartz from illegal mines and forced labor. To ensure PV remains a sustainable

energy option, we must ensure that PV supply chains are free from unethical activities such as using illegal mining and forced labor.

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# Chapter 6 Conclusions and major contributions

PV is critical for electricity generation in the US and globally. It is expected that the transition from fossil fuels to sustainable clean energy such as PV will decarbonize the energy system and mitigate the carbon footprint of fossil fuels. However, this transition from conventional energy to PV faces severe challenges, such as the carbon footprints of manufacturing solar technologies and possible material shortages for PV manufacturing. This dissertation focused on the leading commercialized PV technology (Si PV) and an emerging PV technology (OPV). We investigated the materials and resource availability necessary for making Si PV in the next ten years. We also quantified the carbon footprint and the cumulative energy demand (CED) of providing the primary raw materials needed for Si PV manufacturing. Besides Si PV, we used LCA, green chemistry, toxicity assessment, analytical chemistry, and material flow analysis to determine the environmental hotspots of the fullerene ( $C_{60}$ ) production process required for OPV manufacturing. We evaluated the environmental, cost, and chemical hazard impacts.

### 6.1 Sustainable design for OPV manufacturing

 $C_{60}$  is often used as an electron acceptor in OPV manufacturing, even though it significantly contributes to OPV's carbon footprint. Existing  $C_{60}$  production processes are energy-intensive and require a large amount of hazardous materials. We evaluated the environmental, cost, and chemical hazards of existing  $C_{60}$  purification methods (e.g., chromatography, crystallization, & complexation) and determined the complexation process as the baseline with the lowest environmental, cost, and chemical hazard impacts. We used LCA and identified that more than 95% of the cumulative energy demand of the purification process comes from the solvent (1,2,4-trimethylbenzene - TMB) used in the baseline method. Therefore, green chemistry principles were employed to determine potential greener replacements for highly toxic TMB. Potential alternative solvents were identified based on hazardous scores and  $C_{60}$  solubility scores. Plant-based solvents, such as olive oil, linseed oil, and sunflower oil as well as petroleum-based solvents, such as toluene and xylene, were determined as the potential replacements due to their high  $C_{60}$  solubility and low toxicity scores compared to TMB. The toxicity score of toluene and xylene was estimated based on the EPA software, TEST. However, TEST is not useful for evaluating the toxicity of plant-based solvents and nanoparticles such as  $C_{60}$ . So, a series of singular and combined toxicity tests were conducted based on EPA protocols to quantify the individual toxicity of  $C_{60}$ , TMB, linseed oil, olive oil, and sunflower oil and the combined toxicity of dissolved  $C_{60}$  in each solvent.

In the second Chapter, we showed that linseed oil, olive oil, sunflower oil had much lower toxicity effects than TMB on tested species (*Daphnia Magna*). The C<sub>60</sub> did not show toxicity effects. However, dissolved C<sub>60</sub> was toxic. The highest toxicity was for dissolved C<sub>60</sub> in TMB, while the minimum toxicity was for C<sub>60</sub> in olive oil. The maximum toxicity among solvents was for TMB, and the minimum was for sunflower oil. Olive oil was identified as the potential alternative replacement for TMB based on the singular and combined toxicity assessment.

The third Chapter evaluated the environmental, cost, and chemical hazards of using potential alternative solvents for  $C_{60}$  synthesis. We used an iterative approach to conduct experiments to compare the  $C_{60}$  production rate and the  $C_{60}$  purity of methods using potential replacements for TMB. With the iterative approach, we continuously monitored  $C_{60}$  production rates and  $C_{60}$  purity in each experiment and revised the process using LCA and green chemistry

principles. Even though olive oil had the lowest toxicity score among the potential alternative solvents, the environmental, cost, and chemical hazards of using olive oil were higher than purification processes using other potential alternative solvents. Xylene was identified as the greener alternative solvent for TMB since the purification process had the lowest environmental, cost, and chemical hazard impacts.

#### 6.2 Material requirement for Si PV manufacturing and associated environmental impacts

Supplying required materials for Si PV manufacturing and associated socio-environmental impacts can be a big challenge for energy system decarbonization. Chapter 4 quantified the amount of materials (e.g., glass, metallurgical-grade silicon (MG-Si), aluminum, silver, copper, lead, and tin) needed for Si PV laminate manufacturing. We used a bottom-up approach to evaluate the material necessary to manufacture each sub-Si PV technology (e.g., Al-BSF, mono facial and bifacial PERC, mono facial and bifacial HJT, and perovskite/Si tandem). The highest material demand was for glass and MG-Si. More than 74 billion metric tons of solar glass and three billion metric tons of MG-Si will be necessary for the next ten years to manufacture enough Si PV to meet the global expected electricity generation from PV.

The highest raw material demand was determined for quartz. Chapter five evaluated the resource availability and the purity of quartz used for MG-Si and solar glass production. High-quality quartz (>98% silica) is required for MG-Si production, and industrial-grade quartz (95% silica) is needed for solar glass manufacturing. We determined the location and the purity of available quartz resources globally. We also employed LCA to model silica sand production and quantify the carbon footprint and the cumulative energy demand (CED) of quartz mining, silica sand extraction, and MG-Si production. The purity had a significant effect on the carbon footprint

and CED of MG-Si. This is due to the excessive energy necessary to remove impurities from quartz deposits with lower quality. Providing silica sand for MG-Si production had about 36% more carbon footprint than supplying silica sand from high-quality resources. We also determined that some global leading Si PV producers do not have access to domestic high-quality quartz resources and are highly dependent on high-quality foreign resources. Meanwhile, this Chapter highlighted the possibility of supplying silica sand from illegal mines for Si PV manufacturing. This can increase Si PV impacts on the local environment and communities. We proposed using a kind of third-party certifications to monitor the Si PV supply chain to ensure that illegal quartz is not used for Si PV manufacturing and consumers buy ethical PV products.

#### **6.3** Conclusion

This dissertation focused on the environmental evaluation of OPV and Si PV manufacturing. The manufacturing process of OPV, the emerging solar technology, requires sustainable modifications before large-scale production.  $C_{60}$  is needed for OPV manufacturing and has a significant impact on OPV carbon footprint. We used LCA, green chemistry, toxicity assessment, analytical chemistry, and material flow analysis to identify the environmental hotspots of the  $C_{60}$  production process and determine alternative greener production processes. The final replacements were evaluated based on environmental, cost, and chemical hazard impacts. We also considered Si PV, the most commercialized solar technology, and quantified materials necessary for Si PV manufacturing in the next ten years. The resource availability, quality of raw material deposits, and the possibility of supplying raw materials from illegal mines were assessed. Results from this dissertation can be used to mitigate the environmental, cost, and chemical hazards of OPV manufacturing before large-scale production. Results also highlighted the potential material shortage for Si PV manufacturing in the next couple of years as well as the importance of using

third-party certification to monitor the Si PV supply chain besides improving the MG-Si production process to use low-quality quartz without increasing Si PV carbon footprint.

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APPENDICES

# **APPENDIX A: Supplementary Information for Chapter 2**

# A1. Solvent properties

concerce non reference [1] except those were mentioned in the bracket.					
Substrate	C <sub>60</sub> solubility (g/L) [179]	C <sub>70</sub> solubility (g/L) [179]	Market price (USD/L)	Viscosity (mPA s)	Water solubility (g/L)
Brassica oil	0.19	1.03	166 [4]	N.A.	N.A.
Castor oil	0.39	0.64	78 [4]	1000 [280]	N.A.
Cedar oil	51.8 (343)	N.A.	173 [4]	5000 [180]	N.A.
Corn oil	0.61	1.96	86.4 [4]	35.4 [180]	N.A.
Grapeseed oil	0.37 (293)	N.A.	200 [8]	46.6 [281]	N.A.
Linseed oil	53.1 (328)	1.2	94 [281]	48 [280]	N.A.
O-xylene	9.3 [282]	15.6 [5]	110.5 [281]	0.6 [6]	0.02 [283]
Olive oil	23.6 (323)	1.04	119 [281]	58.2 [4]	N.A.
Peanut oil	0.75	0.85	189 [281]	73 [280]	N.A.
Soybean oil	0.86	0.75	88.9 [281]	60 [280]	N.A.
Sunflower oil	6.91	1.83	19.6 [281]	48.8 (299) [280]	N.A.
Tetralin	15.7	12.3	119 [281]	2 [284]	Very poor
					[285]
Toluene	8.7	1.4	63 [281]	0.6 [284]	0.53 [286]
TMB	17.9	N.A.	64.2 [281]	2[10]	0.057 [287]
Walnut oil	0.48 (293)	1.39	100 [285]	42.9 (299) [281]	N.A.

**Table A1.** Physical properties and market price for conventional solvents and essential oils. All solubility and viscosity were reported at 298 K except when mentioned in parentheses. Data was collected from reference [1] except those were mentioned in the bracket.

# A2. Toxicity studies for fullerenes

Fullerene preparation Method	Ecotoxicity test condition	Findings	Ref
Dissolve fullerenes in THF following by filtration and evaporation 30-min sonication of fullerenes in DI water	<ul> <li>EPA protocol</li> <li>Acute test for 48 h</li> <li>Daphnia magna</li> </ul>	<ul> <li>LC<sub>50</sub> of fullerenes in THF method: 0.46 ppm</li> <li>LC<sub>50</sub> of fullerenes in sonication method: 7.9 ppm</li> </ul>	[76]
Stir fullerene in water for 2 months under the sunlight	<ul> <li><i>D. magna</i></li> <li>Acute test for 48 h</li> <li>Chronic test for 21 d</li> </ul>	<ul> <li>No LC<sub>50</sub> for acute tests</li> <li>Reduced offspring production in chronic tests</li> <li>Sonication of fullerene in water increased the toxicity of fullerene</li> <li>For the environmental purpose, sonication and adding THF are not acceptable.</li> </ul>	
Dissolve fullerene in THF	- Juvenile Largemouth Bass	- Significant lipid peroxidation after 48 h exposure to 0.5 ppm nC <sub>60</sub>	[288]
Dissolve fullerene in THF	- E. coli and B. Subtilis	<ul> <li>Antimicrobial properties against both E coli and B Subtilis</li> <li>Minimum inhibitory concentration for E coli: 0.5-1 mg/L of C<sub>60</sub></li> <li>Minimum inhibitory concentration for E Subtilis: 1.5-3 mg/L of C<sub>60</sub></li> </ul>	[134] 3.
<ul> <li>Dissolved fullerenes in THF</li> <li>Suspended fullerenes in water (stirring for weeks)</li> </ul>	<ul> <li>US EPA</li> <li>48-h acute tests on <i>D.</i> magna</li> </ul>	<ul> <li>LC<sub>50</sub> of THF-fullerenes: 0.8 ppm</li> <li>LC<sub>50</sub> of stirred C<sub>60</sub>: more than 35 ppm</li> </ul>	[75]
<ul> <li>Dissolved fullerenes in Ethanol (EthOH/nC<sub>60</sub>)</li> <li>Suspended fullerenes in water by mixing for 2 weeks (auq/nC<sub>60</sub>)</li> </ul>	- Micronucleus tests	- Auq/nC <sub>60</sub> showed higher genotoxicity than EthOH/nC <sub>60</sub>	[289]
- Suspended fullerenes in natural and artificial freshwater by mixing for 4 weeks at 20 oC	- 24 and 48 h acute tests on <i>D. magna</i>	<ul> <li>Less than 20% death in <i>daphnids</i> for concentrations lower than 10 mg/L</li> <li>Highly variable death rates in <i>daphnids</i> for concentrations higher than 10 mg/L</li> </ul>	[74]

**Table A2.** Summary of previous acute tests for fullerenes

# A3. Experimental setup for toxicity tests



**Figure A1.** Experimental setup for culturing daphnids and acute tests. Fluorescent light with the intensity of  $70\pm5$  foot candles and a 16 h photoperiod was used. Daphnids grew up in reconstituted water with mentioned pH, alkalinity, and hardness at room temperature. Twenty offspring daphnids ( < 24 h old) were used for each concentration (five daphnids in each beaker).

# A4. Hazardous scores

Substrate	Health	Flammability	Reactivity	Special	Hazardous	NFPA
					score	source Ref
Brassica oil	1	1	0	0	0.67	[290]
Castor oil	0	0	0	0	0	[291]
Cedar oil	2	2	0	0	1.33	[291]
Corn oil	0	1	0	0	0.33	[291]
Grapeseed oil	1	1	0	0	0.67	[292]
Linseed oil	0	1	0	0	0.33	[291]
O-xylene	3	3	0	0	2	[293]
Olive oil	1	1	0	0	0.67	[293]
Peanut oil	0	1	0	0	0.33	[291]
Soybean oil	0	1	0	0	0.33	[291]
Sunflower oil	0	1	0	0	0.33	[291]
Tetralin	2	2	1	0	1.5	[293]
TMB	2	2	0	0	1.33	[293]
Toluene	3	3	0	0	2	[293]
Walnut oil	1	1	0	0	0.67	[290]

**Table A3.** Chemical hazards (NFPA) and calculated hazardous score using the method from Lee

# A5. Pre-screening results

Toxicant	% of toxicants in	% of dead
	100-mL beakers	daphnids
Linseed oil	30	100
	3	0
	0.3	0
Olive oil	30	100
	3	40
	0.3	0
Sunflower oil	30	100
	3	20
	0.3	0
TMB	10	100
	1	100
	0.1	20

Table A4. Mortality of *daphnids* for prescreening tests after 48 h exposure to toxicants

# A6. Physiochemical properties of fullerenes

Table A5. Physiochemical properties of suspended fullerenes (m	naximum and minimum
concentrations) in the test medium.	

Media	C <sub>60</sub> concentration (ppm)	Average size (nm)*	Zeta potential (ξ, mV)
Reconstituted water (auq/nC <sub>60</sub> )	176	584	38.6
	11	132	-38.6
$C_1$ (TMB + auq/nC <sub>60</sub> )	176	731	-38.8
	11	395	-37.9
$C_2$ (Linseed oil + auq/nC <sub>60</sub> )	176	454	-38.8
	11	215	-38.3
$C_3$ (Olive oil + auq/nC <sub>60</sub> )	176	715	-38.0
	11	452	-38.4
$C_4$ (Sunflower oil + auq/nC <sub>60</sub> )	176	755	-37.9
	11	81	-38.6

# A7. C<sub>60</sub> concentration measurments

The concentration of suspended  $C_{60}$  in stock and dilutions was calculated by measuring the absorption at 335 nm in UV-VIS spectroscopy (Figure A2). First, absorption of standard solutions was done to extrapolate fitting equation (Eq. 1) from fitting curve (Figure A2.a). Then, the concentrations of  $C_{60}$  in stock and dilutions (x in Eq. A1) were calculated by measuring the absorptions of extracted C60 at 335 nm (y in Eq. A1) (Figure A2-b).

$$y = 0.1047x + 0.0551$$
 Eq. (A1)

Where y is the absorbance at 335 nm and x is the concentration of  $C_{60}$  in toluene.



**Figure A2.** Absorption measurements at 335 nm in UV-VIS spectroscopy of (a) standard solutions ( $C_{60}$  in Toluene) and the fitting curve, (b) extracted  $C_{60}$  as explained in sec 2.3

# A8. Singular toxicity



**Figure A3.** Light-microscopic images of *daphnids* after 48 h exposition to  $auq/nC_{60}$  at different concentrations. The dead *D. magna* is shown to provide a comparison between live and dead *daphnids*.



**Figure A4.** pH measurements and dose-response curves after 48-h acute tests for (a) 1,2,4-TMB, (b) linseed oil, (c) olive oil, (d) sunflower oil.



Figure A5. Essential oil structures for (a) linseed oil, (b) olive oil, and (c) sunflower oil

## A9. Gas Chromatography – Mass Spectroscopy (GC-MS) analysis

The GC-MS analysis was performed to quantify the composition of fatty acids in watersoluble fraction (WSF) of linseed oil, olive oil, and sunflower oil using an Agilent 7890B GC/ triple quadrupole mass spectrometer 7010B (Agilent, Santa Clara, CA). One µL of the derivatized sample was injected in a split mode (1:20) to quantify total oil in WSF. All injections were performed with an injector temperature of 250 °C and a flow rate of 1.2 mL/min helium. Separation was achieved on an Agilent J&W VF5ms column (30 m x 0.25 mm x 0.25 µm) (Agilent, Santa Clara, CA) using the following temperature profile: 40°C for 2 min; 25°C min-1 to 200°C; 4°C min-1 to 230°C; 40°C min-1 to 320°C; 320°C for 5 min. Ionization employed 70 eV electron ionization, and the mass spectrometer was operated in scanning mode with the first quadrupole with a scan range of m/z 45 to 450. FAMEs were identified by comparing their mass spectra and retention time to the Supelco 37 component FAME mix (Sigma-Aldrich, St. Louis, MO). TargetLynx (Waters Corporation, Milford, MA) was used for data analysis after exporting the original MassHunter data file into NetCDF format, then converting it into water. Quantification was based on the peak response of the total ion chromatogram (TIC) for the respective FAMEs normalized to the internal standard (glyceryl triheptadecanoate) (C17:0 methyl ester at 12.8 min).

Solvent extraction was used to prepare samples for GC-MS analysis. A mixture of chloroform/methanol (2:1) with 90 mg/L butylated hydroxytoluene (BHT) (0.01% (w/v)) and 1 mL formic acid (1% (v/v)).


Figure A6. The chromatogram of sunflower oil – GC-MS



Figure A7. The chromatogram of the WSF of sunflower oil – GC-MS

## A10. Combined toxicity

Table A6. C<sub>60</sub> impacts on the toxicity of Baseline (TMB) and alternative solvents (essential oils)

Solvent	C <sub>60</sub> concentration (mg/L)					
	Antagonism effect	Additive effect	Synergism effect			
TMB	≤ 11	$22 \leq \ldots \leq 88$	176≤			
Linseed oil			11 ≤			
Olive oil	≤ 44	88	176 ≤			
Sunflower oil	≤ 11	22	44 ≤			

#### A11. Dilution factors

Dilution factors could have a role in the toxic consequence effects of fullerenes. Contaminated fullerenes could be released into the environment in many ways at different concentrations. For example, the concentration of fullerenes in effluent water from treatment plants was estimated from few ng/L to  $67 \mu g/L$  [294,295], while this concentration could be higher if fullerenes are used in "down-the-drain" consumer products (e.g., C<sub>60</sub> in essential oils as a human supplement or in pharmaceutical products) or accidental spills happen during the manufacturing process (e.g., fullerene purification steps). Dilution factors in the environment significantly vary among countries from five (Morocco) to 33,500 (Canada) [296]. For instance, dilution factors were estimated between 10 to 40 for India, Iran, Iraq, Italy, and Belgium, 100 to 500 for Australia, China, and the USA, and higher than 500 for Canada, Russia, and Brazil [296]. In this study, these estimated dilution factors (five to 33,500) were also considered to design the combined toxicity. The concentration of C<sub>60</sub> in TMB and essentials oils before releasing to the environment was presented in Tables A7 and A8.

	C <sub>60</sub> concentration in solvents (mg/L)	Reference
Human supplement (C <sub>60</sub> in olive oil)	800	[123]
Fullerene purification (TMB)	11,400	[160]
Fullerene purification (linseed oil)	33,200	Calculation based on [160]and
Fullerene purification (olive oil)	14,800	C <sub>60</sub> solubility in the essential
Fullerene purification (sunflower oil)	4,300	oils.

**Table A7.** C<sub>60</sub> concentrations in essential oils (human supplements) and TMB (in fullerene purification step)

	combined toxicity tests	)	
	This study	literature	Ref
C <sub>60</sub> in TMB	41 to 656	5 to 33,500	[296
C <sub>60</sub> in linseed oil	34 to 544		
C <sub>60</sub> in olive oil	Under the detection limit		
C <sub>60</sub> in sunflower oil	15 to 240		

**Table A8.** Dilution factors for mixtures (the "fixed-ratio-design" approach was used to conduct combined toxicity tests)

# **APPENDIX B: Supplementary Information for Chapter 3**

### **B1. Detailed methodology**



**Figure B1.** The material flow of complexation method (Nagata et al. [58]) - line shows the system boundary that was considered for LCA



**Figure B2.** The material flow of crystallization method (Kwok et al. [297]) - line shows the system boundary that was considered for LCA



**Figure B3.** The material flow of crystallization method (Grushko et al. [298]) - line shows the system boundary that was considered for LCA



Figure B4. Material flow for modified baseline



Figure B5. Material flow for P3 and P4 (alternative purification methods using olive oil)



Figure B6. Material flow for P5 and P6 (alternative purification methods using linseed oil)

## B2. Data source for life-cycle assessment

	Description	Ref.
1 2 4-trimethylbenzene	Co-production of mesitylene, xylenes, and benzene	[299]
	from naphtha cracking	
1,8-Diazabicyclo	Synthesis of bicyclic amidines from caprolactam by	[104]
(5.4.0)undec-7-ene	using acrylonitrile	
Linseed oil	Process modification from Refined sunflower oil	[300]
	(pressing), at processing, Agri-footprint 5.0;	
	Linseed seed, Ecoinvent 3	
Olive oil	Process modification from olive production,	[300][301]
	Ecoinvent 3 [300], based on information on olive	
	oil production[301]	
Centrifuge	Required energy was estimated based on using	[302]
Mixer	industrial-scale equipment.	[303]
Pump		[304]
Ultrasonic bath		[305]
Ultrasonic probe		[306]

Table B1. Data sources for material and energy used in inventory analysis

## **B3.** Green chemistry principles

Principle #	Description	How we used
1	Waste prevention instead of cleaning waste after it is formed	N/A
2	Maximize the incorporation of all used materials into the final products	N/A
3	Using substances that have little or no toxicity for human health and the environment	We categorized potential solvents based on toxicity scores and identified alternative solvents with lower toxicity.
4	Design safer chemicals with lower environmental toxicity	We identified non-hazardous alternative solvents to avoid toxifying the final products.
5	Use less solvents	We categorized potential solvents based on their fullerene solubility to reduce the amount of solvents necessary for fullerene purification.
6	Minimizing energy	N/A
7	Using renewable feedstock	We identified plant-based alternative solvents besides petroleum-based solvents.
8	Avoiding unnecessary derivatization	N/A
9	Catalytic reagents are better than stoichiometric reagents	N/A
10	Avoid using undegradable chemicals	N/A
11	In-process monitoring to avoid generating hazardous materials	We used analytical chemistry (HPLC-UV) to monitor the impurity.
12	Safer substrates for accident prevention	We determined alternative non-hazardous solvents to reduce accidental release risk.

 Table B2. Green chemistry principles [24]

## **B4.** Prescreening solvents to identify replacements for TMB

Toxicity scores were calculated using TEST software for all solvents except plant-based solvents.

# in	Solvent	CAS #	Toxici	Normalized	C <sub>60</sub>	Normalize	Ref
Figure	Solvent		tv	toxicity	solubili	d Ceo	iten.
3. 5.			(LC50)	score	tv (g/L)	solubility	
			(100)	50010	·) (g =)	score	
			mg/L			~~~~	
<b>–</b>	1,2,4-trimetyilbenzene	95-63-6	8.64	0.238	17.9	0.337	[56]
s ir ple	Olive oil	8001-25-0	54,500	$3.78 \times 10^{-5}$	23.6	0.444	[56,168]
ent our rea	Linseed oil	8001-26-1	17,400	1.19× 10 <sup>-4</sup>	53.1	1	[56,168]
olv he j a	Xylene	95-47-6	12.3	0.167	9.3	0.18	[282]
S ±	Toluene	108-88-3	17.3	0.119	8.7	0.16	[56]
1	Sunflower oil	8001-21-6	160,00	$1.29 \times 10^{-5}$	6.91	0.130	[56,168]
			0				
2	1,1,2,2-	79-34-5	95.9	0.021	5.3	0.10	
	tetrachloroethane						
3	2-methylthiophene	554-14-3	30.4	0.068	6.8	0.13	
4	Benzene	71-43-2	23.6	0.087	2.9	0.06	
5	Cyclohexene (C6H10)	110-83-8	23.4	0.088	1.21	0.023	
6	quinoline (C9H7N)	91-22-5	15.9	0.129	7.2	0.14	
7	1,4-dimethylbenzene	106-42-3	12.3	0.167	5.9	0.11	
8	chlorobenzene	108-90-7	11.4	0.181	5.7	0.11	
9	1,3-dimethylbenzene	108-38-3	12.3	0.167	2	0.03	
10	1-bromotetradecane	112-29-8	9.01	0.229	6.2	0.12	
	(CH3(CH2)13Br)						
11	1,Bdimethylbenzene	620-14-4	7.29	0.283	7.3	0.14	
12	Tetralin	119-64-2	7.40	0.278	15.7	0.296	[56]
13	1,2,3,5-	95-93-2	5.97	0.345	20.8	0.392	[30]
	tetrarnethylbenzen						
14	1,2,3,5-	527-53-7	5.97	0.345	18	0.34	
	tetramethylbenzene						
15	1,2-dimethylbenzene	615-60-1	5.46	0.377	6	0.1	
16	tribromomethane	75-25-2	4.74	0.435	5.64	0.106	
17	1,2-dichlorobenzene	95-50-1	4.98	0.414	17	0.32	
18	1-methylnaphthalene	90-12-0	4.79	0.430	33	0.62	
19	1 chloronaphthalene	90-13-1	2.96	0.696	52	0.98	
-	(C10H7Cl)						-
20	dimethyl naphthalenes	571-58-4	3.26	0.632	36	0.68	-
21	1,2,3-tribromopropane	96-11-7	3.34	0.617	8.31	0.156	
	(C3H5Br3)						
22	1,5,9-	706-31-0	2.32	0.888	7.4	0.14	
	cyclododecatriene	4004 51 5		0.001		0.1	4
23	1,5,9-	4904-61-4	2.30	0.896	7	0.1	5.5.63
	cyclododecatriene						[56]
24	(CI2HI8)	120.02.1	2.06	1.00	12	0.24	4
24	1,2,4-trichlorobenzene	120-82-1	2.06	1.00	13	0.24	
1	(C6H3Cl3)	1		1	1		1

Table B3. Solvent toxicity scores and C<sub>60</sub> solubility.

#### **B5.** Chemical hazards analysis

The chemical hazard score of materials was calculated based on NFPA 704 standard scores (Table B4) and Eq. B1 [104]. The chemical hazard score of purification processes was quantified using data from Table B4 and Eq. B2 (Table B5). The amount of materials was compiled from experiments. The chemical hazard score of purification processes was normalized on the basis of the baseline score (Table B5).

$$H_{m} = \frac{(\text{Health}) + (\text{Flammability}) + 0.5(\text{Reactivity} + \text{Special})}{3} \qquad \text{Eq. (B1)}$$

$$H_{p} = \sum_{i}^{n} (H_{m})_{i} \times M_{i}$$
 Eq. (B2)

Where  $H_m$  is the hazardous score of materials used in each purification process. Health, Flammability, Reactivity, and Special are NFPA standard scores (Table B4).  $H_p$  is the hazardous score of the purification process (Table B5). n is the number of materials, and M is the amount of materials used in each purification process.

Solvents	Health (Blue)	Flammability (Red)	Reactivity (Yellow)	Special (white)	Hazardous score	Ref.
1,2,4-trymethilbenzene (TMB)	2	2	0	0	1.33	[293]
Acetic acid (AcOH)	3	2	0	0	1.67	[293]
DBU (1,8- Diazabicyclo[5.4.0]undec-7- ene)	3	1	0	0	1.33	[307]
Heptane	1	3	0	0	1.33	[293]
IPA	2	3	0	0	1.67	[293]
Linseed oil	0	1	0	0	0.33	[308]
Olive oil	1	1	0	0	0.67	[308]
Toluene	3	3	0	0	2.00	[293]
Xylene	3	3	0	0	2.00	[293]

**Table B4.** Solvent chemical hazard scores based on NFPA.

Table B5. Chemical hazard scores for fullerene purification methods

Method	Hazard score for all used materials	Normalized scores
Baseline	522.9	100
Modified baseline	298.8	57
P <sub>3</sub> (alternative using olive oil)	978.8	187
P4 (alternative using olive oil)	785.6	150
P <sub>5</sub> (alternative using linseed oil)	388.7	74
P <sub>6</sub> (alternative using linseed oil)	175.3	34
P7 (alternative using xylene)	80.76	15
P <sub>8</sub> (alternative using toluene)	70.28	13

#### B6. Life cycle cost analysis

Cost analysis was conducted based on the  $C_{60}$  production rate and life cycle cost of  $C_{60}$  production [104]. The production rate was calculated using recorded data from experiments and then were normalized on the basis of the baseline (Table B6). The life cycle cost was conducted using life cycle inventory. We picked out energy materials and then calculated the cost based on the amount of energy materials and price for each process (Table B7 and B8). Cost metric values were calculated using equal weighting for normalized production rates and life cycle cost scores (Table B9).

Process	Time (hr)	Rate	Normalized Production Rate
Described and	(III) 5.12	(Kg/III)	
Baseline	5.12	0.195	I
Modified baseline	5.27	0.190	0.972
P <sub>3</sub> (alternative using olive oil)	5.45	0.183	0.939
P <sub>4</sub> (alternative using olive oil)	5.25	0.190	0.975
P <sub>5</sub> (alternative using linseed oil)	5.45	0.183	0.939
P <sub>6</sub> (alternative using linseed oil)	5.25	0.190	0.975
P <sub>7</sub> (alternative using xylene)	5.27	0.190	0.972
P <sub>8</sub> (alternative using toluene)	5.27	0.190	0.972

Table B6. Production rate

Table B7. The price of energy materials in life cycle inventory

Ref.
309]
310]
310]
310]
311]

Table B8. life cycle cost analysis

Process	Normalized score
Baseline	1.00
Modified baseline	0.583
P <sub>3</sub> (alternative using olive oil)	2.30
P <sub>4</sub> (alternative using olive oil)	2.22
P <sub>5</sub> (alternative using linseed oil)	1.00
P <sub>6</sub> (alternative using linseed oil)	0.408
P7 (alternative using xylene)	0.252
P <sub>8</sub> (alternative using toluene)	0.197

Table B9. Cost metric values of processes

Process	Cost Metric Value
Baseline	1
Modified baseline	0.778
P <sub>3</sub> (alternative using olive oil)	1.62
P <sub>4</sub> (alternative using olive oil)	1.60
P <sub>5</sub> (alternative using linseed oil)	0.970
P <sub>6</sub> (alternative using linseed oil)	0.691
P7 (alternative using xylene)	0.612
P <sub>8</sub> (alternative using toluene)	0.584

#### **B7.** Environmental impact assessment

LCA was conducted in SimaPro 9.1.0.7 [169] for the environmental evaluation of purification processes. The environmental analysis was based on equal weighting of various environmental impacts, including CED, GWP, WD, and E-Factor, for the baseline and potential alternative methods. We used the TRACI 2.1 V1.05 method for Global warming potential (GWP) analysis, Cumulative Energy Demand V1.11 method for energy assessment, (Water Scarcity) V1.00 method for water demand (WD) analysis [170], and E-Factor calculation [171].

Methods	CED (MJ)	Normaliz ed CED	GWP (kg CO <sub>2</sub> eq)	Normalized GWP	WD (m <sup>3</sup> )	Normalized WD	E- Factor	Normali zed E- Factor	Normaliz ed LCA score
Baseline	8,950	100	308	100	9.0	100	381	100	100
Modified baseline	5,110	57	176	57	5.0	57	217	57	57
P <sub>3</sub>	30,10 0	337	1,790	581	94	1061	1090	287	567
P <sub>4</sub>	28,30 0	316	1,710	554	88	1003	816	215	522
P <sub>5</sub>	15,40 0	172	823	267	33	370	641	168	244
P <sub>6</sub>	6,770	76	348	113	13	147	325	85	105
P <sub>7</sub>	3,180	36	195	63	9.0	102	46.5	12	53
P <sub>8</sub>	2,510	28	151	49	7.0	78	39.9	10	41

 Table B10. LCA analysis details

### **B8.** Sustainability assessment

Sustainability evaluation was based on the average of chemical hazard scores (Table B5), cost scores (Table B9), and environmental impact scores (Table B10).

Methods	Environmental impacts score (GWP, CED, WDI, E-Factor)	Chemical hazard score	Cost score
Baseline	100	100	100
Modified baseline	57	57	78
P <sub>8</sub> (alternative using toluene)	41	13	58
P <sub>7</sub> (alternative using xylene)	53	15	61
P <sub>5</sub> (alternative using linseed oil)	244	74	97
P <sub>6</sub> (alternative using linseed oil)	105	34	69
P <sub>3</sub> (alternative using olive oil)	567	187	162
$P_4$ (alternative using olive oil)	522	150	160

Table B11. environmental, cost, and chemical hazard scores of the baseline and replacements

# **APPENDIX C: Supplementary Information for Chapter 4**

#### C1. PV installation growth in the next decade



Figure C1. Annual PV installation from 2021 to 2031 (Adapted from 2020 DNV-GL Energy Transition Outlook [13])

We considered potential improvements for each Si PV technology based on industrial outlooks (e.g., ITRPV 2021 [39]). Linear regression was used to extrapolate technology improvements for each year between 2021 and 2031. For example, HJT Si efficiency is estimated to be 22.3% in 2026 based on the efficiency in 2021 and 2031 (Table 4.1).



Figure C2. SHJ Si PV efficiency calculation

The amount of materials needed for Si PV manufacturing was calculated using information from Table 4.1 and the following equation.

$$A = \sum_{i=1}^{n} \frac{P_i \times M_i \times S_i \times G_i}{E_i} \times C$$
 Eq. (C1)

$$T = \sum_{i=1}^{N} A_i$$
 Eq. (C2)

Where A is the quantity of materials needed for manufacturing Si PV sub technology in the next n years.  $P_i$  is PV installations in the year i,  $M_i$  is market share in the year i,  $S_i$  is a reduction factor for Si wafer thickness in the year i,  $G_i$  is a reduction factor for solar glass thickness in the year i,  $E_i$  is the efficiency in the year i, C is the amount of current materials necessary for making PV, and T is the total materials needed for Si PV manufacturing.





**Figure C3.** Materials necessary for Si PV laminate manufacturing in the US and the rest of the world for the baseline (A),  $S_1$  (B),  $S_2$  (C), and  $S_3$  (D)

C3. Materials necessary for manufacturing Si PV sub technology in the US and the rest of the world



Figure C4. Materials necessary for Al-BSF Si PV laminate manufacturing in the US for S<sub>3</sub>



Figure C5. Materials necessary for Al-BSF Si PV laminate manufacturing in the rest of the world for  $S_3$ 



**Figure C6.** Materials necessary for PERC Si PV and HJT Si PV laminate manufacturing in the US for  $S_3$  (a) monofacial c-Si PV, (b) monofacial mc-Si PV, (c) bifacial c-Si PV, (d) bifacial mc-Si PV



**Figure C7.** Materials necessary for PERC Si PV and HJT Si PV laminate manufacturing in the rest of the world for  $S_3$  (a) monofacial c-Si PV, (b) monofacial mc-Si PV, (c) bifacial c-Si PV, (d) bifacial mc-Si PV



Figure C8. Materials necessary for perovskite/silicon tandem PV laminate manufacturing in the USA and the rest of the world for  $S_3$ 



Figure C9. The material intensity for manufacturing Si PV laminate globally

# **APPENDIX D: Supplementary Information for Chapter 5**

#### D1. Previous environmental impact assessment of silicon photovoltaic (Si PV)

Life cycle assessment (LCA) has been widely used to evaluate Si PV manufacturing's environmental impacts. This section summarized Si PV LCA studies that included global warming potential (GWP) (Figure D1 and D2) and cumulative energy demand (CED) (Figure D3 and D4).



Figure D1. The GWP of monocrystalline Si PV manufacturing based on studies from 1990 to 2016 [312–329]



**Figure D2.** The GWP of multi-crystalline Si PV manufacturing based on studies from 1990 to 2018 [181,314–318,320–324,329–341]



**Figure D3.** The CED of multi-crystalline Si PV manufacturing based on studies from 1990 to 2016 [181,314–317,322–324,330–333,335,337–345]



**Figure D4.** The CED of multi-crystalline Si PV manufacturing based on studies from 1990 to 20 [181,314–316,321–324,330,331,334,341,342,344–347]

	Reference
Studies ignored quartz purity	[181,314-

Table D1. Analysis of previous studies on environmental impact assessment of Si PV.

Studies ignored quartz purity	[181,314– 318,320,321,323,325,329,330,333– 337,339–341,344,346–354]
Studies ignored quartz mining and silica sand extraction	[313,320,332,340,342,355]



## D2. Previous environmental impact assessment of silicon photovoltaic (Si PV)

Figure D5. Quartz mining (High-quality)



Figure D6. Silica sand extraction (High-quality)



Figure D7. Quartz mining (industrial grade and low-quality)



Figure D8. Silica sand extraction (magnetic separation technique)



Figure D9. Silica sand extraction (flotation separation technique)



Figure D10. Silica sand extraction (gravity separation technique)



Figure D11. Metallurgical grade silicon (MG-Si) production

### D3. Data source for life-cycle assessment

	Details	Ref.
Quartz mining	It was modeled based on the process of quartz mining and silica sand	[205,206,356-
and silica sand	extraction in Unimin Corporation, the global leading silica sand	359]
extraction	producer. They have 21 active quartz deposits throughout the USA	-
(industrial-	with 41 million annual productions. Their annual silica sand	
grade quartz)	production includes 83.35% high-quality quartz, and the rest consists	
	of 6.43% magnetic separation and 10.22% flotation.	
Quartz mining	It was modeled based on a quartz mine that used three separation	
and silica sand	techniques: 1/3 magnetic, 1/3 flotation, and 1/3 gravity.	
extraction (low-		
quality quartz)		
MG-Si	We used quartz with different purity for MG-Si production: high-	[4,256,360]
	quality, industrial-grade, and low-quality quartz mines.	
Distance for	For silica sand export to China, we assumed distance between foreign	[4,361,362]
silica sand	resources and the closest port to the target MG-Si producer.	
	- Australia to China (Shanghai): 4,584 km	
	<ul> <li>Cambodia to China (Yunnan province): 1,500 km</li> </ul>	
	<ul> <li>Malaysia to China (Beihai port): 2,485 km</li> </ul>	
	- North Korea to China (Yantai port): 408 km	
	<ul> <li>Pakistan to China (Xinjiang province): 700 km</li> </ul>	
electricity	Regional electricity was used for modeling electricity in China. We	[258,269,363–
	divided China into six regions (Figure 5. 9): Northwest, North,	365]
	Northeast, East, South, and Center. The leading province producer was	
	used as the representative of each region: Northwest (Xinjiang), North	
	(Beijing), Northeast (Liaoning), East (Fujian), South (Yunnan), Center	
	(Sichuan).	

**Table D2.** Data sources for materials and energy used in the inventory analysis

## D4. Silica sand application

Industrial silica sand (95% silica) is used for hydraulic fracturing, glass making, foundry, filtration, and manufacturing semiconductor and solar panels (Figure D12). Industrial silica sand production has tripled since 2010.



**Figure D12.** Applications of a) sand and b) industrial sand. It was compiled based on the USGS report [199] and ISSST2020 conference [366]

#### D5. Illegal silica sand extraction in India



Figure D13. Illegal silica sand trades in 2016 [245–247,263–266]

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