Supplementary Information (SI) for Green Chemistry.
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PHA Biocomposites from Lignocellulose: Scalability and Sustainability Analyses through Dynamic Simulation, LCA, and TEA

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Supplementary Information

Fig. 3 in the main text shows the process block diagram. Here, the lignocellulose pretreatment process is discussed as follows. In the first stage of the fractionation process, biomass is fed to a pretreatment reactor and mixed with diluted sulfuric acid (18 mg acid/dry g of biomass; 99% of it is recovered and recycled within the process, minimizing its make up requirements) that catalyzes the hydrolysis reaction at a temperature of 158 °C. Steam at 13 bar is used in this stage to maintain the temperature. Most of the hemicelluloses are converted into oligosaccharides within a short residence time of 5 min. The resulting slurry is sent to a second stage of fractionation, the oligomer conversion step, where most of the oligosaccharides from the first stage are converted into C5 monosaccharides at 130 °C and a residence time of 20-30 min. The slurry is then flashed at atmospheric pressure. After the flash, the slurry containing 30 wt% total solids is sent to a conditioning reactor, where water and ammonia are added to dilute the solids to approximately 20 wt% and raise the pH to 5–6 to ensure miscibility for hydrolysis. The slurry is cooled to 75 °C after a total conditioning residence time of 30 min. Ammonia helps to avoid sugar losses and eliminate the solid-liquid separation steps. This makes ammonia a more economical alternative to lime, due to reduced sugar loss and lower capital costs.

Fig. S1 shows the integrated cultivation and starvation fermenters. The nutrient medium for microorganisms comprises three solutions added to a vitamin mix. The first solution (medium 1) contains 50 ml of distilled water with KH_2PO_4 (2.3 g) and $Na_2HPO_4 \cdot 2H_2O$ (2.9 g). The second solution (medium

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2) contains 920 ml of distilled water as well as NH_4Cl (1 g), $MgSO_4 \bullet 7H_2O$ (0.5 g), $CaCl_2 \bullet 2H_2O$ (0.01 g), $MnCl_2 \bullet 4H_2O$ (0.005 g), $NaVO_3 \bullet H_2O$ (0.005 g), trace elements (5 ml) and agar (20 g). The third solution (medium 3) contains 20 ml of distilled water and ferric ammonium citrate (0.05 g). These three solutions are added together with 5 ml of the vitamin solution. These three solutions are added together with 5ml of the vitamin solution as follows. The 100 ml vitamin solution has riboflavin (10 mg), thiamine-HCl • $2H_2O$ (50 mg), nicotinic acid (50 mg), pyridoxine-HCl (50 mg), Ca-pantothenate (50 mg), biotin (0.1 mg), folic acid (0.2 mg), and Vitamin B_{12} (1 mg). The overall solution is autoclaved for 15 mins at 121 ^{o}C before cooling. The growth of microorganism (*C. necator)* and under starving conditions, PHA accumulation can happen sequentially, as shown in **Fig. S1**.

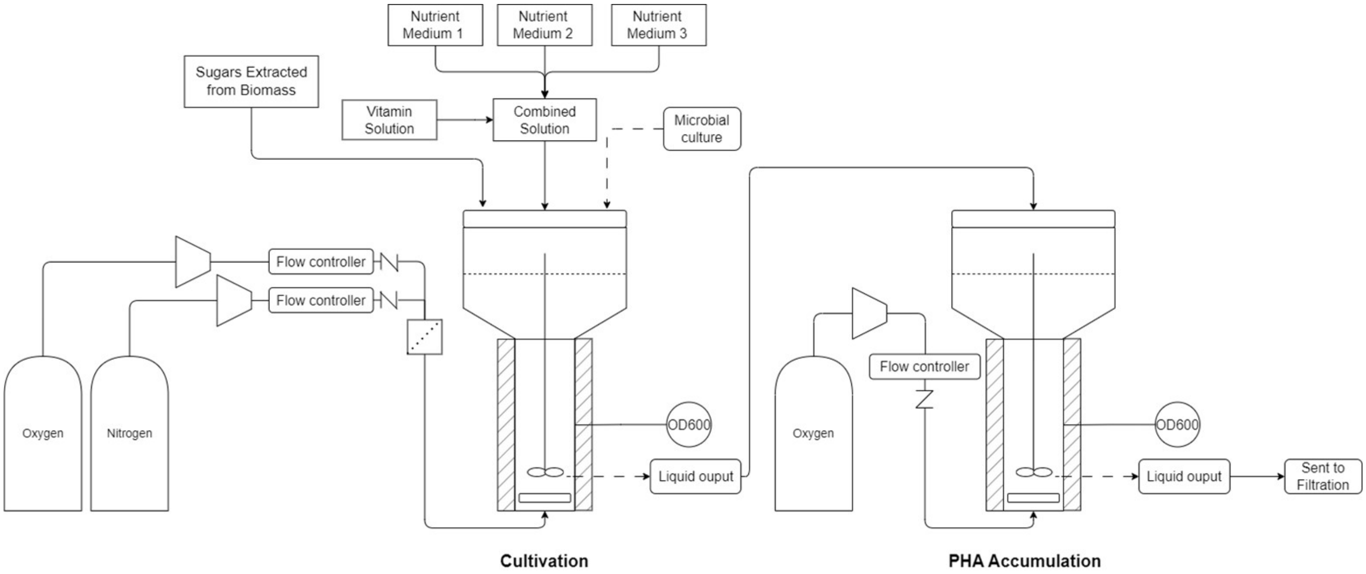

Fig. S1. Sequential reactors with cultivation (nutrient-enriched or feast) and copolymer accumulation (starvation or famine) in two reactors, respectively.

Table S1 shows the properties, standards, analytical equipment used to test these properties, PHA properties before and after reinforcement, and a comparison with fossil-based polypropylene. The PHA composites can meet the same properties as the fossil-derived polypropylene after reinforcing PHA copolymers with (0.1 – 0.2 w/w) cellulose fiber biofillers.

Table S1. Property standards, analytical equipment for testing PHA properties before and after reinforcement, and benchmarking against fossil-based polypropylene.

Properties	University Facilities	Standards	PHA copolymers	PHA biocomposites	Fossil-derived polypropylene
Melt flow index	Extrusion Plastometer	ASTM D1238 - 20 ISO 1133	10 – 100 g/10mins	10 – 30 g/10mins	1 – 50 g/10mins
Density	Density Gradient Technique	ASTM D1505 - 18 ISO 1183-2	1.18 g/cm³	1.25 g/cm³	0.9 g/cm³
Glass transition temperature	Differential Scanning Calorimeter	ASTM D3418 ISO 11357-1	6 °C	12 °C	8.4 °C (homopolymer)
Thermal stability	Thermogravimetric analysis	ASTM E1131 ISO11358	170 °C	250 °C	160 – 170°C
Molecular weight	Gel Permeation Chromatography	ASTM D6474 ISO 13885	50,000 – 1,000,000 g/mol	500,000 – 2,000,000 g/mol	5000 – 1,000,000 g/mol
Tensile strength	Universal Testing Machine	ASTM D1708, ASTM D638 – 14 ISO 20753 ISO 527-2	5 – 14 Mpa	20 – 40 MPa	30 – 50 Mpa
Young's modulus	Universal Testing Machine	ASTM D638 ISO 20753 ISO 527-2	500 MPa	1000 – 1500 MPa	1000 – 1800 MPa

Fig. S2 shows the engineering stress-strain tensile test and FTIR results, explained in the caption.

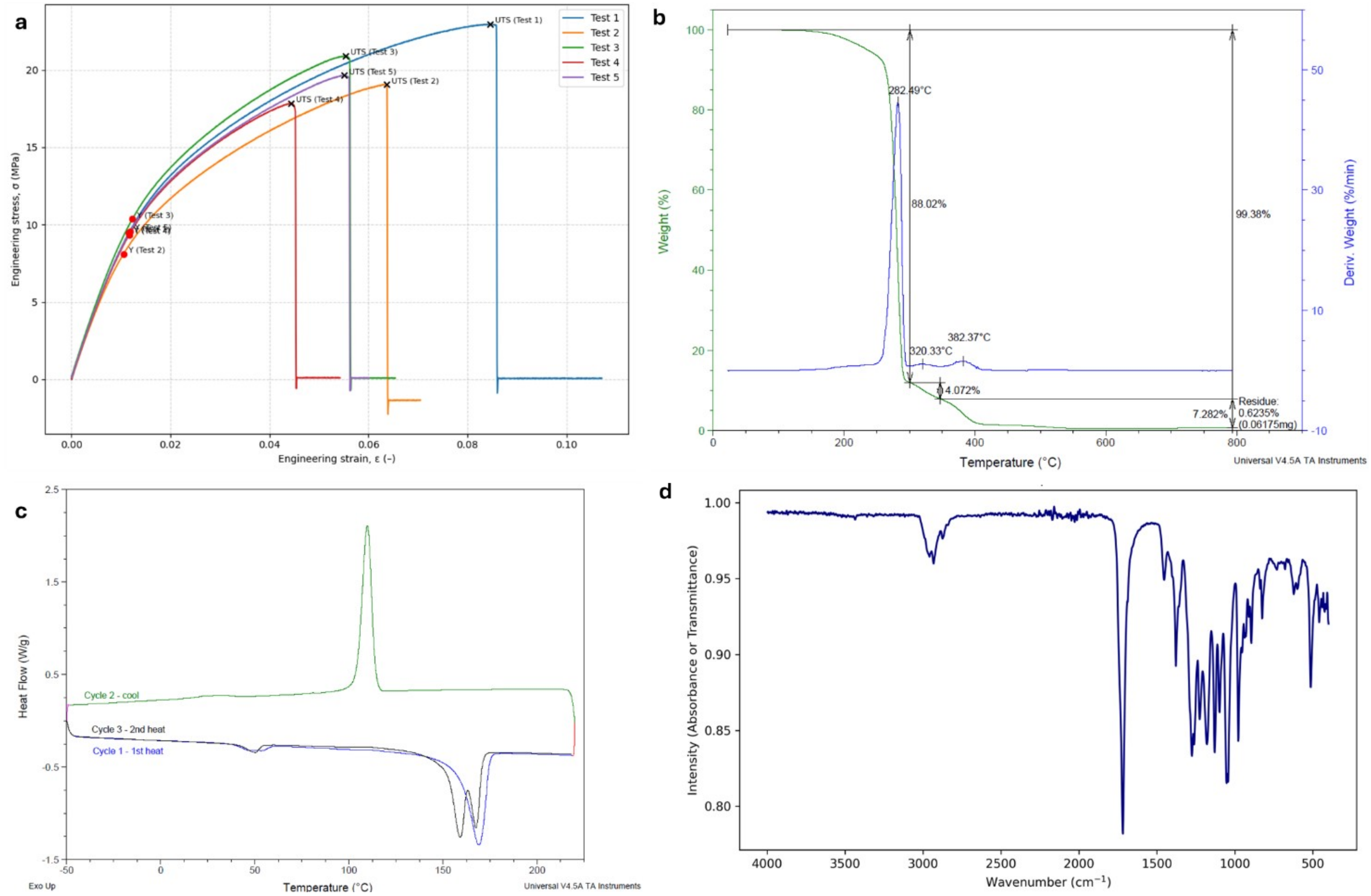

Fig. S2. a) Engineering stress-strain tensile test of PHA-biocomposites: Young's modulus: 0.96 – 1.01 GPa (Mean: 0.98 GPa) (Polypropylene benchmark: 1 – 1.8 GPa); Yield strength: 8.2 – 10.4 MPa (Mean: 9.37 MPa) (Polypropylene benchmark: 20 – 30 MPa); Ultimate tensile strength: 17.9 – 23.0 MPa (Mean: 20.1 MPa) (Polypropylene benchmark: 30 – 50 MPa); Elongation at break: 4.4% – 8.5% (Mean: 6.1%) (Polypropylene benchmark: 2 – 10%). **b**) Thermogravimetric analysis (TGA) of PHA. A 9.90 mg sample was heated from room temperature to 800°C at a ramp rate of 10°C/min under an inert nitrogen atmosphere. The onset of thermal degradation is at 282.49°C. **c**) Differential scanning calorimetry (DSC) thermograms of PHA using a heat–cool–heat (HCH) protocol. They show a melting endotherm at 168.98°C (ΔH_m = 97.69 J/g), crystallisation exotherm at 109.79°C (ΔH_c = 84.57 J/g), glass transition at 41–50°C and a melting endotherm at 159.13°C (ΔH_m = 84.16 J/g). **d**) ATR-FTIR characterisation of PHA samples. Fourier-transform infrared transmittance spectra of PHA specimens, acquired from 4,000 to 400 cm^{-1}: weak aliphatic C–H stretching of $–CH_3$ and $–CH_2–$ groups at 2,975 and 2,934 cm^{-1}; an intense, narrow ester carbonyl (C=O) stretch centred at ~1,720 cm^{-1}, the established marker of the crystalline phase of PHA;

methyl bending modes at 1,453 and 1,380 cm⁻¹; and a series of coupled C–O–C and C–O stretching vibrations at 1,278, 1,228, 1,180, 1,130, 1,100 and 1,055 cm⁻¹, among which the sharp 1,228 cm⁻¹ band and the 980 cm⁻¹ C–CH₃ stretch are characteristic of a highly ordered crystalline lamellar structure.

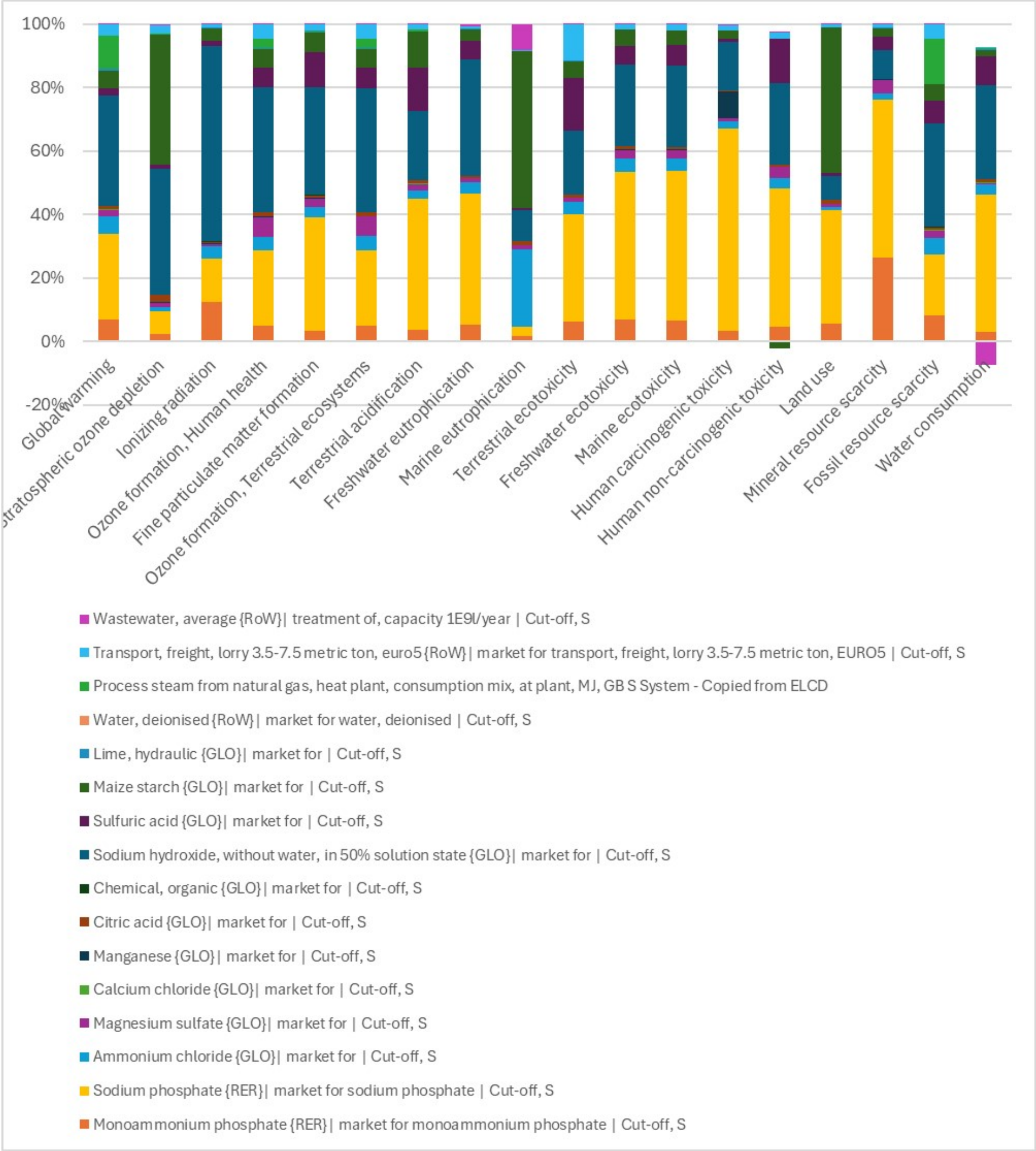

Fig. S3. Hotspot analysis of inventories towards each LCIA category of the ReCiPe (M) (H) method.

Table S2. ReCiPe (M) (H) LCIA by inventories for 1 kg PHA biocomposite production.

Impact category	Unit	Total	Monoammonium phosphate {RER}| market for monoammonium phosphate | Cut-off, S	Sodium phosphate {RER}| market for sodium phosphate | Cut-off, S	Ammonium chloride {GLO}| market for | Cut-off, S	Magnesium sulfate {GLO}| market for | Cut-off, S	Calcium chloride {GLO}| market for | Cut-off, S	Manganese {GLO}| market for | Cut-off, S	Citric acid {GLO}| market for | Cut-off, S	Chemical, organic {GLO}| market for | Cut-off, S	Sodium hydroxide, without water, in 50% solution state {GLO}| market for | Cut-off, S	Sulfuric acid {GLO}| market for | Cut-off, S	Maize starch {GLO}| market for | Cut-off, S	Lime, hydraulic {GLO}| market for | Cut-off, S	Water, deionised {RoW}| market for water, deionised | Cut-off, S	Process steam from natural gas, heat plant, consumption mix, at plant, MJ, GB S System - Copied from ELCD	Transport, freight, lorry 3.5-7.5 metric ton, euro5 {RoW}| market for transport, freight, lorry 3.5-7.5 metric ton, EURO5 | Cut-off, S	Wastewater, average {RoW}| treatment of, capacity 1E9l/year | Cut-off, S
Global warming	kg CO2 eq	1.51E+00	1.06E-01	4.09E-01	8.01E-02	3.38E-02	4.10E-04	1.39E-03	1.54E-02	1.08E-03	5.25E-01	3.34E-02	8.55E-02	9.24E-03	5.36E-05	1.57E-01	5.41E-02	2.17E-03
Stratospheric ozone depletion	kg CFC11 eq	1.41E-06	3.46E-08	9.77E-08	2.11E-08	1.95E-08	1.14E-10	4.08E-10	3.38E-08	2.40E-10	5.58E-07	2.04E-08	5.80E-07	8.42E-10	4.93E-11	4.41E-09	3.52E-08	5.55E-09
Ionizing radiation	kBq Co-60 eq	9.32E-02	1.15E-02	1.28E-02	3.64E-03	8.01E-04	1.38E-05	1.07E-04	5.04E-04	2.92E-05	5.74E-02	1.70E-03	3.61E-03	9.75E-05	3.60E-06	2.09E-05	9.68E-04	9.37E-05
Ozone formation, Human health	kg NOx eq	3.50E-03	1.72E-04	8.34E-04	1.53E-04	2.15E-04	1.01E-06	5.79E-06	4.07E-05	2.52E-06	1.38E-03	2.20E-04	2.03E-04	1.38E-05	1.23E-07	1.06E-04	1.52E-04	8.03E-06
Fine particulate matter formation	kg PM2.5 eq	3.33E-03	1.06E-04	1.19E-03	1.10E-04	8.99E-05	1.03E-06	5.52E-06	3.15E-05	1.40E-06	1.13E-03	3.73E-04	2.02E-04	5.73E-06	1.28E-07	1.89E-05	5.77E-05	6.04E-06
Ozone formation, Terrestrial ecosystems	kg NOx eq	3.56E-03	1.76E-04	8.49E-04	1.56E-04	2.18E-04	1.02E-06	5.89E-06	4.13E-05	2.81E-06	1.39E-03	2.25E-04	2.07E-04	1.40E-05	1.25E-07	1.07E-04	1.57E-04	8.16E-06
Terrestrial acidification	kg SO2 eq	8.75E-03	3.24E-04	3.60E-03	2.51E-04	1.71E-04	3.41E-06	6.58E-06	8.75E-05	3.16E-06	1.90E-03	1.20E-03	9.81E-04	1.44E-05	2.98E-07	5.34E-05	1.32E-04	1.48E-05
Freshwater eutrophication	kg P eq	7.00E-04	3.74E-05	2.89E-04	2.46E-05	8.81E-06	2.16E-07	6.25E-07	4.88E-06	2.55E-07	2.57E-04	3.94E-05	2.69E-05	9.34E-07	2.10E-08	6.46E-10	5.59E-06	4.29E-06
Marine eutrophication	kg N eq	2.73E-04	4.24E-06	8.03E-06	6.68E-05	3.27E-06	1.33E-08	3.53E-08	4.19E-06	2.00E-08	2.62E-05	1.63E-06	1.35E-04	6.17E-08	2.17E-09	2.84E-08	5.15E-07	2.28E-05
Terrestrial ecotoxicity	kg 1,4-DCB	4.94E+00	3.06E-01	1.68E+00	1.86E-01	7.10E-02	2.57E-03	1.88E-03	3.78E-02	1.15E-03	1.00E+00	8.12E-01	2.65E-01	3.60E-03	1.86E-04	3.67E-04	5.64E-01	7.35E-03
Freshwater ecotoxicity	kg 1,4-DCB	1.13E-01	7.71E-03	5.26E-02	4.69E-03	2.90E-03	2.06E-05	3.75E-04	8.20E-04	2.87E-05	2.91E-02	6.62E-03	5.86E-03	3.94E-05	5.65E-06	2.35E-07	1.66E-03	1.84E-04
Marine ecotoxicity	kg 1,4-DCB	1.48E-01	9.93E-03	6.96E-02	6.04E-03	3.74E-03	2.98E-05	5.51E-04	1.05E-03	3.75E-05	3.79E-02	9.72E-03	6.89E-03	5.61E-05	7.32E-06	1.55E-05	2.52E-03	2.44E-04
Human carcinogenic toxicity	kg 1,4-DCB	2.82E-01	9.15E-03	1.80E-01	6.20E-03	2.37E-03	2.22E-05	2.37E-02	9.78E-04	5.01E-05	4.33E-02	3.24E-03	7.14E-03	8.51E-05	7.45E-06	3.12E-05	4.39E-03	9.11E-04
Human non-carcinogenic toxicity	kg 1,4-DCB	2.30E+00	1.12E-01	1.04E+00	8.28E-02	8.34E-02	9.71E-04	1.56E-03	1.72E-02	6.12E-04	6.12E-01	3.36E-01	-5.27E-02	1.65E-03	1.07E-04	8.12E-05	4.86E-02	1.17E-02
Land use	m2a crop eq	1.62E-01	9.05E-03	5.81E-02	1.68E-03	1.14E-03	2.44E-05	4.50E-05	2.21E-03	1.15E-05	1.21E-02	1.61E-03	7.43E-02	3.56E-05	1.23E-06	8.12E-05	1.54E-03	1.12E-04
Mineral resource scarcity	kg Cu eq	1.85E-02	4.88E-03	9.26E-03	3.35E-04	7.68E-04	2.54E-06	5.59E-05	5.54E-05	1.86E-06	1.67E-03	7.95E-04	4.86E-04	3.72E-05	4.89E-07	1.81E-06	1.56E-04	3.51E-05
Fossil resource scarcity	kg oil eq	4.02E-01	3.24E-02	7.83E-02	2.02E-02	9.84E-03	8.54E-05	3.01E-04	3.40E-03	7.01E-04	1.31E-01	2.87E-02	2.05E-02	1.03E-03	1.44E-05	5.75E-02	1.77E-02	4.79E-04
Water consumption	m3	3.95E-02	1.37E-03	2.01E-02	1.46E-03	2.77E-04	1.33E-05	8.04E-06	4.81E-04	1.77E-05	1.38E-02	4.23E-03	9.31E-04	2.32E-05	1.15E-04	2.50E-05	1.07E-04	-3.47E-03