Graphene synthesis – Supporting information

S 1. Life cycle inventory analysis: Lab scale graphene production

This first section presents the life cycle inventory for all graphene production processes analysed in the main paper: electrochemical exfoliation of graphite rods, chemical oxidation of graphite and subsequent thermal or chemical reduction and chemical vapour deposition. Data are measured directly from processes running at lab scale considering the full capacity use of the lab equipment.

The study covers the standard LCA impact categories suggested in the ILCD methodology (Joint Research Centre (EU Commission), *ILCD handbook* 2010). Those categories fall into three main areas of protection: human health, natural environment and natural resources. In detail they are: global warming potential, ozone depletion, human toxicity (carcinogenic and non-carcinogenic), particulate matter, ionising radiation, photochemical ozone formation, acidification, terrestrial eutrophication, fresh water eutrophication, fresh water ecotoxicity, resources depletion (water and fossil and mineral).

S 1.1 Electrochemical exfoliation of graphite

This first section introduces the inventory of materials and LCA results for the electrochemical exfoliation processes at laboratory scale.

Production of 1 g of Graphene		KOH 15 V	KOH 9 V	CH$_3$COONa 15 V	CH$_3$COONa 9 V
Electricity	MJ	1.85	3.88	2.49	3.14
Graphite	g	3.91	3.01	3.50	3.58
Potassium hydroxide	g	1.12	1.12	-	-
Sodium acetate	g	-	-	1.64	1.64
Sodium hydroxide	g	-		-	-
Water (deionised)	kg	0.67	0.5	0.63	0.49

Table S1 – LCI of electrochemical exfoliations for the production of 1g of graphene

	ELECTROCHEMICALLY EXFOLIATED MATERIALS			
	CH3COONa 15 V	CH3COONa 9 V	KOH 15 V	KOH 9 V
Global Warming Potential [kg CO2-Equiv.]	4.2E-01	5.2E-01	3.3E-01	6.1E-01
Ozone Depletion [kg CFC 11-Equiv.]	2.9E-10	3.6E-10	2.2E-10	4.3E-10
Human toxicity, cancer [CTUh]	1.2E-10	1.4E-10	9.7E-11	1.7E-10
Human toxicity, non-canc. [CTUh]	1.5E-08	1.9E-08	1.2E-08	2.2E-08
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	1.4E-04	1.7E-04	1.0E-04	2.1E-04
Ionising radiation, human health effect model, [kg U235 eq]	9.5E-01	1.2E+00	7.3E-01	1.4E+00
Photochemical ozone formation,[kg NMVOC]	8.1E-04	1.0E-03	6.3E-04	1.2E-03
Acidification [Mole of H+ eq.]	2.1E-03	2.6E-03	1.6E-03	3.1E-03
Terrestrial eutrophication, [Mole of N eq.]	2.9E-03	3.6E-03	2.2E-03	4.2E-03
Freshwater eutrophication, [kg P eq]	3.5E-07	4.4E-07	3.7E-07	4.8E-07
Ecotoxicity [CTUe]	1.3E-02	1.6E-02	1.0E-02	1.9E-02
Resources depletion, water [kg]	4.7E-01	5.9E-01	4.3E-01	6.9E-01
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	5.8E-06	6.0E-06	6.5E-06	5.2E-06

Table S2 – Electrochemical exfoliation: comparison for all impact categories. KOH 15 V is the least impacting in 12 out of the 13 impact categories. Colours show the relative contribution from red (higher impact) to green (lower impact)

Table S1 shows that the lowest energy consumption is in relation with higher voltages, due to a quicker exfoliation process, but also that, for the same reason, the KOH electrolyte requires less electricity than CH₃COONa. It also shows that KOH consumes slightly more water (that dissociates into hydrogen and oxygen) and that to higher voltages correspond higher water consumption. Even though the KOH 9V process seems to be the most efficient in terms of material conversion (3 g of graphite for 1 g of graphene) this cannot be verify as most of the graphite in the rods is graphitic binder (up to 70% according to the manufacturer) that is either not exfoliated into graphene.

Life cycle impacts are shown in Table S2. The KOH 15 V route achieves the lowest impact in almost all impact categories analysed. In the fresh water eutrophication category, the potassium hydroxide (KOH) 15 V performs slightly worse than the sodium acetate (CH3COONa) 15 V process. KOH uses less electricity, but it consumes more deionised water, and this is what makes it more impacting in this category. However, due to data aggregation it is not possible to understand why the deionised water drives water eutrophication. When considering the overall water depletion, the KOH 15 V is still the least impacting process. This shows that the larger part of water consumption is consumed during the electricity generation (hydroelectricity; water input to condensers at thermal generating stations) and that the water consumed (Table S1) in the graphene synthesis is small in comparison.

S 1.2 Chemical oxidation processes

This section introduces the inventory of materials and LCA results for the chemical oxidation processes at laboratory scale. These results exclude the acid neutralisation as, in an optimised scenario, the sulphuric acid will not be neutralised but reused. A section with the results including the acid neutralisation is provided at the end of this section for completeness of results. Table S3 shows the lowest energy consumption for GO2 that also needs a similar or lower quantity of input materials if compared with the other four methods.

Graphite Oxide (1 g)	GO1	GO2	GO3	GO4	GO5	
Electricity	0.03	0.01	0.11	0.09	0.02	MJ
Graphite	0.71	0.71	0.77	0.73	0.80	g
Nitric acid (98%)	-	-	-	9.9	24.4	g
Sulphuric acid aq. (96%)	32.8	30.2	248	23.4	-	g
Water (deionised)	232	223	423	455	270	g
Potassium chlorate	-	-	-	8	-	g
Hydrogen peroxide (100%)	2.6	1.24	6.69	-	-	g
Sodium nitrate	0.36	0.36	0.39	-	-	g
Potassium permanganate	2.14	2.14	3.08	-	-	g
Hydrochloric acid	-	-	2.28	2.16	-	g
Sodium chlorate	-	-	-	-	6.80	g
Calcium hydroxide*	24.7	22.8	187	23.5	14.3	
* used for neutralising 100% of the acid(s) used						

Table S3 – LCI of the chemical oxidation of graphite for the production of 1 g of graphene oxide

The GO3 route is showing the largest energy and material inputs proving to be inefficient if compared to the other methods. It requires heating a larger quantity of chemicals to a temperature just below 100 °C hence a higher quantity of energy. GO1 needs the same temperature for the reaction to occur, but the quantity of material heated is much lower.

GO4 and GO5 happen at ambient temperature, but the reaction time is much longer, 96 and 24 hours respectively and the all the energy consumption is due to stirring. GO2 is the least energy consuming

mostly because the reaction happens in less than one hour at low temperature (around 35 °C). GO2 and GO1 are also the processes that require less graphite to obtain 1 gram of graphite oxide and they are the most similar among all of them in terms of energy and material inputs.

	GOx MATERIALS				
	GO1	GO2	GO3	GO4	GO5
Global Warming Potential [kg CO2-Equiv.]	5.3E-02	4.6E-02	2.8E-01	1.1E-01	1.1E-01
Ozone Depletion [kg CFC 11-Equiv.]	8.7E-12	6.7E-12	2.9E-11	2.5E-09	1.2E-09
Human toxicity, cancer [CTUh]	2.2E-10	1.9E-10	1.4E-09	6.3E-09	4.4E-09
Human toxicity, non-canc. [CTUh]	4.3E-09	3.3E-09	2.3E-08	1.3E-08	6.5E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	1.5E-05	1.3E-05	9.6E-05	3.7E-05	1.3E-05
Ionising radiation, human health effect model, [kg U235 eq]	1.4E-02	1.4E-02	2.2E-02	4.2E-02	3.0E-02
Photochemical ozone formation,[kg NMVOC]	8.3E-05	7.1E-05	4.2E-04	1.9E-04	1.2E-04
Acidification [Mole of H+ eq.]	3.3E-04	2.9E-04	2.1E-03	6.3E-04	2.1E-04
Terrestrial eutrophication, [Mole of N eq.]	2.4E-04	2.0E-04	1.0E-03	6.2E-04	4.3E-04
Freshwater eutrophication, [kg P eq]	1.1E-07	8.9E-08	3.8E-07	3.8E-05	2.1E-05
Ecotoxicity [CTUe]	4.5E-03	4.0E-03	2.9E-02	5.4E-01	2.9E-01
Resources depletion, water [kg]	1.9E-04	1.5E-04	7.1E-04	4.3E-02	2.6E-02
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	1.2E-06	1.2E-06	1.5E-06	2.0E-06	1.5E-06

Table S4 – Chemical oxidation comparison: GO2 is the least impacting material in 12 out of 13 categories

This is also reflected in the LCA comparison of all chemical oxidations (Table S4). GO1 and GO2 are very similar with GO2 being the least impacting process in 12 categories out of 13. GO4 is the most impacting process together with GO3. Even if GO3 requires larger input quantities, GO4 turns out to be the more impacting in 7 categories (due to the use of both sulphuric and nitric acid and potassium chlorate), although GO3 remains the most problematic for the GWP (the most important – see S 1.5). Acidification is less problematic for GO5 because it uses nitric acid instead of sulphuric acid.

S 1.3 – Chemical and thermal reduction processes

This section introduces the inventory of materials and LCA results for the chemical and thermal reduction processes at laboratory scale. In Table S5 it is possible to see how, at lab scale, the thermal reduction (rGO2T) consumes less electricity. This is happening because each chemical reduction batch could process only a limited amount of GO (around 7 g), requires more material inputs (although uses less GO material) and uses a hot plate that it is less insulated than the tube furnace (more heat losses). Thermal reduction can theoretically process more than 10 times as much material in a single batch.

Reduced Graphite Oxide (1 g)	rGO2C	rGO2T	
Ammonia	0.34	-	g
Electricity	0.38	0.28	MJ
Graphite Oxide	1.25	1.67	g
Water (deionised)	163	-	g
Hydrazine	1.38	-	g
Methanol	10	-	g
Argon	-	14	g

Table S5 – LCI of the chemical reduction of graphite oxide for the production of 1g of graphene

When comparing the environmental impacts for the life cycle of the chemical and thermal reductions performed on GO2 (the least impacting GO) to obtain rGO2C and rGO2T, the thermal reduction shows lower impacts on 12 out of 13 impact categories (Table S6).

	GO2x REDUCED MATERIALS IMPROVED LAB SCENARIO	
	rGO2C	rGO2T
Global Warming Potential [kg CO2-Equiv.]	0.15	0.09
Ozone Depletion [kg CFC 11-Equiv.]	4.6E-11	3.8E-11
Human toxicity, cancer [CTUh]	6.2E-11	4.6E-11
Human toxicity, non-canc. [CTUh]	5.5E-09	4.7E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	4.1E-05	3.7E-05
Ionising radiation, human health effect model, [kg U235 eq]	0.2	0.1
Photochemical ozone formation,[kg NMVOC]	2.5E-04	2.0E-04
Acidification [Mole of H+ eq.]	7.2E-04	6.8E-04
Terrestrial eutrophication, [Mole of N eq.]	8.1E-04	5.6E-04
Freshwater eutrophication, [kg P eq]	3.0E-07	1.6E-07
Ecotoxicity [CTUe]	9.4E-03	6.9E-03
Resources depletion, water [kg]	0.14	0.10
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	1.5E-06	2.0E-06

Table S6 – rGO2T and rGO2C comparison: rGO2T is the least impacting. This table includes the oxidation process

rGO2C is less impacting the resource depletion (fossil and mineral) as it requires less GO to produce a gram of graphene (1.67 g Vs 1.25 g), potentially showing to be a less effective oxidation process. These results are be valid also for all other GOs as the reductions processes used would be the same.

S 1.4 – Chemical Vapour Deposition (CVD)

This section introduces the inventory of materials and LCA results for the chemical vapour deposition processes at laboratory scale. Table S7 shows the LCI of CVD graphene productions of 1 g of graphene OR 1 cm^2. It also shows that CVD 1 uses less electricity and precursor gas as it requires a lower temperature and a smaller reaction time (5 min for CVD 1 and 20 min for CVD 2), but it also uses argon while in CVD 2 hydrogen is required.

	1 g			1 cm^2		
	CVD 1	CVD 2		CVD 1	CVD 2	
Copper	203	203	kg	0.016	0.016	g
Electricity	831,944	1,282,508	MJ	64.1	98.8	kJ
Hydrogen	37	68	kg	0.003	0.005	g
Methane	-	112	kg	-	0.001	g
Argon	15,896	-	kg	1.224	-	g
Hexane	27	-	kg	0.002	-	g

Table S7 – LCI of CVD graphene for the production of 1 g OR 1 cm^2 of graphene

	CVD IMPROVED LAB SCENARIO				
	1g CVD 1	1g CVD 2		1cm^2 CVD 1	1cm^2 CVD 2
Global Warming Potential [kg CO2-Equiv.]	1.2E+05	1.7E+05		8.9E-03	1.3E-02
Ozone Depletion [kg CFC 11-Equiv.]	8.0E-05	1.2E-04		6.2E-12	9.5E-12
Human toxicity. cancer [CTUh]	3.3E-05	4.8E-05		2.6E-12	3.7E-12
Human toxicity. non-canc. [CTUh]	5.2E-03	7.2E-03		4.0E-10	5.5E-10
Particulate matter/Respiratory inorganics. [kg PM2.5-Equiv.]	4.1E+01	6.1E+01		3.1E-06	4.7E-06
Ionising radiation. human health effect model. [kg U235 eq]	2.8E+05	4.1E+05		2.1E-02	3.2E-02
Photochemical ozone formation.[kg NMVOC]	2.3E+02	3.4E+02		1.8E-05	2.6E-05
Acidification [Mole of H+ eq.]	6.0E+02	9.0E+02		4.6E-05	6.9E-05
Terrestrial eutrophication. [Mole of N eq.]	8.0E+02	1.2E+03		6.2E-05	9.2E-05
Freshwater eutrophication. [kg P eq]	8.0E-02	1.1E-01		6.1E-09	8.5E-09
Ecotoxicity [CTUe]	6.4E+03	8.1E+03		4.9E-04	6.2E-04
Resources depletion. water [kg]	1.2E+05	1.8E+05		9.5E-03	1.4E-02
Resource Depletion. fossil and mineral [kg Sb-Equiv.]	6.3E+00	6.4E+00		4.9E-07	4.9E-07

Table S8 – CVD graphene comparison: all impact categories for the production of 1 g OR 1 cm² of graphene. CVD 1 proves to be the least impacting (green) in all impact categories. From a 21% less ecotoxicity to a 35% less ozone depletion. The two CVD processes impact similarly the fossil and mineral resource depletion

Both gases are used to keep the furnace clean from impurities. Nevertheless, the argon usage in CVD 1 is not large enough to counterbalance the larger use of electricity of CVD 2. As shown in Table S8, the impact assessment for the CVD graphene synthesis at lab scale is in favour of the CVD 1 due to its lower operational temperature and higher production rate (thus lower energy consumption). Electricity consumption is the main environmental burden for all impact categories (more than 90%). The fossil and mineral resources depletion category shows similar results for both processes because of a similar use of copper, that is the main driver for this category.

When considering the CVD method using grams as functional unit, is possible to see that the energy needed to produce one gram of graphene via CVD is a million times bigger than that needed to operate the other methods, however, one gram of CVD monolayer graphene would have a surface area of almost 1300 m². Comparing the processes using only the surface area as functional unit would not be possible either as the materials synthesised chemically or electrochemically considerably vary in thickness and weight.

S 1.5 Normalised life cycle environmental impacts

This section only takes into consideration the least impacting materials and excludes the CVD as it is not fundamental for the scope of this comparison. In fact, this section shows a comparison of all impact categories selected to establish which is the most important and, therefore, the one to focus on. To do so, life cycle impacts of laboratory scale graphene production are normalised based on EU-27 2010 person equivalents. Results are plotted in Figure S1. The dominant metric is the climate change (global warming potential) category, with normalised impacts 2 to 3 orders of magnitude greater than other environmental impacts. As such, we primarily focus on GWP impacts in our analysis of results. Weighting sets were also applied and they confirmed the validity of the results as they mostly tend to give to the global warming potential the highest priority.
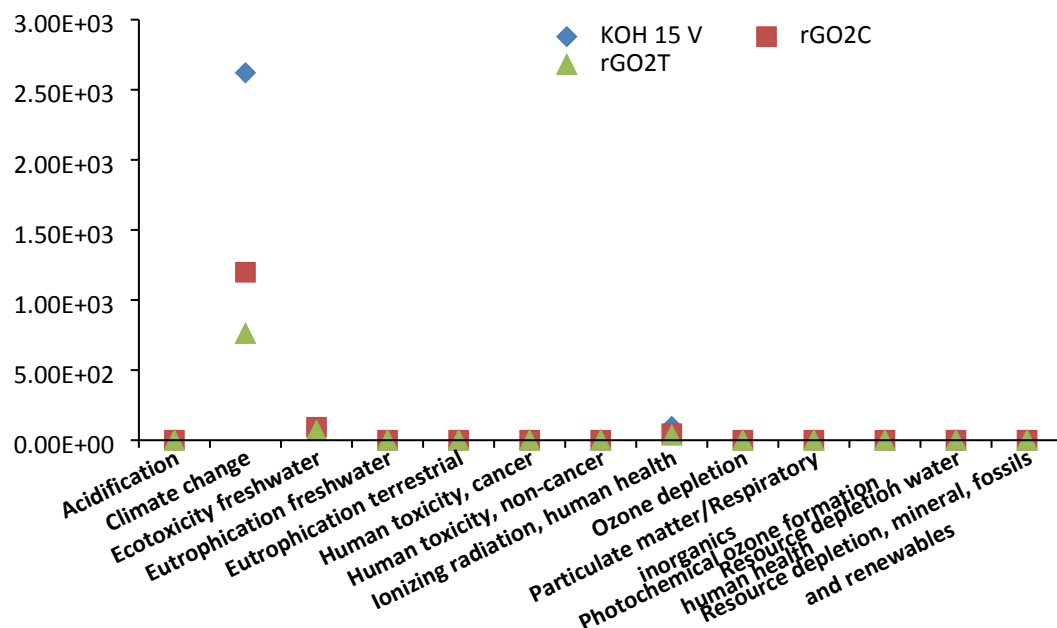
Figure S1: Lab scale scenario results: all impact categories.

An example of set used (created by researchers of the JRC) can be found in: Huppes, G., et al., *Weighting environmental effects: Analytic survey with operational evaluation methods and a meta-method.* The International Journal of Life Cycle Assessment, 2012. **17**(7): p. 876-891.

S2. Commercial scale and decarbonised energy scenarios

This section presents further explanations and more details about the commercial scale scenario and decarbonised scenario. The reason why only sulphuric acid is recycled up to 90% is explained and the LCI of the commercial scale scenario together with the LCIA for both commercial scale and decarbonised energy scenarios are provided.

S 2.1 Sulphuric acid recycling

The wastes are estimated based on the fact that the reaction of $KMnO_4$ + $NaNO_3$ + H_2SO_4 will give approximately $MnSO_4$ + NO_2 + Na_2SO_4 + K_2SO_4 + H_2O. This reaction is non-stoichiometric as the extent of the oxidation is unknown, but it can be estimated using the difference in weight between the graphite and the graphite oxide. Assuming the reaction of $KMnO_4$ will be 100% shifted to the right (no oxidising agent left) and that the additional oxygen needed is given by the sulphuric acid (SO_4^-), it is possible to give a rough estimation of waste quantity as a worst case scenario (no reuse possible).

According to the quantity of sulphuric acid involved and to the reaction performed, about 97% of the acid is used as solvent and does not take part in the reaction. However, the formula used does not consider the graphite oxidation. Some SO_4^- ions intercalate into the graphite layers consuming some of the 97% excess acid. According to the experiments, 1 gram of graphite gains from 20% to 40% more weight when oxidised. Even if assuming all the weight increase being due to the sulphuric acid ions intercalation (while it is mostly due to the oxidising agent), a 40% weight increase equals to 0.4 g of H_2SO_4 that is 0.22 ml (density 1.839 g/ml) or less than 1% of the total acid quantity. Consequently, when including process losses, is reasonable to assume that a reduction of -90% in the acid consumption is possible and still on the conservative side. The acid needs purification from impurities and water (including the water used to wash the GO), but this is not included in the current analysis.

S 2.2 LCI and LCIA for commercial scale and decarbonised energy scenarios

This section includes the LCA results of all impact categories for the most promising materials analysed. The scale it is increased to a possible commercial scale scenario, hence energy inputs are reduced, due to an improved thermal insulation and reuse of some chemicals. In the case of GO2, the acid neutralisation is considered for the portion of the acid that is not reused.

Graphene (1 g)	CVD 1	KOH (15 V)	rGO2C	rGO2T	
Electricity	257	1.85	0.008	0.011	MJ
Graphite	-	2.29	0.89	1.19	g
Copper	203	-	-	-	kg
Hydrogen	37	-	-	-	kg
Argon	15896	-	-	-	kg
Hexane	27	-	-	-	kg
Potassium hydroxide	-	1.12	-	-	g
Water (desalinated; deionised)	-	0.67	0.28	0.37	kg
Ammonia	-	-	0.09	-	g
Hydrazine	-	-	1.38	-	g
Ethanol	-	-	10	-	g
Argon	-	-	-	3.87	g
Sulphuric acid aq. (96%)	-	-	3.78	5.04	g
Hydrogen peroxide (100%)	-	-	1.55	2.07	g
Sodium nitrate	-	-	0.45	0.60	g
Potassium permanganate	-	-	2.68	3.57	g
Calcium hydroxide*	-	-	2.85	3.80	g
* used for acid neutralisation					

Table S9 – LCI for the commercial scale production of 1 g of graphene

For the commercial scale electrochemical exfoliation, the best yield measured among all batches running is used. For the chemical oxidation and reduction, besides sulphuric acid, also ethanol could be reused further, but more experiments are needed to understand up to which percentage. Ethanol is used for rinsing the reduction product thus, reusing it at different rinsing stations with different level of purity for ethanol it is also a possibility not considered in this study. This will significantly contribute in reducing the GWP impact of the reduction process as ethanol, graphite oxide and hydrazine contribute to roughly 30% each.

From Table S9 is clear that, to produce 1 g of graphene, the chemical reduction uses slightly less GO material (in weight) than the thermal reduction (1.25 g Vs 1.67 g). Usually, during the thermal reduction there is a weight loss of about 35 – 40% while in the chemical one it is about 20 – 25% and this means that the latter is a lower performing reduction process that does not remove as much oxygen from the graphite oxide as the thermal reduction does. However, it could also be that some of the graphene carbon atoms form hydrocarbons (methane, ethane, ethane, acetylene) and a smaller quantity of (poly)aromatic compounds (benzene, toluene, xylenes…) and that the weight difference is not only due to a lower oxygen content, but also to a lower content of carbon. Further studies are needed to give a definitive answer on this subject.

Heat losses were considered as function of time: from 10 to 20% heat lost every hour depending on the temperature as to higher temperatures correspond larger losses. Results showed that a loss of heat of around 120% during thermal reduction (the more energy demanding process) generated a variation in GWP of less than 5%.

The process efficiencies are kept as those measured except for the electrochemical exfoliation that uses the best efficiencies obtained from different batches. The decarbonised scenario takes into consideration a future in which almost all electricity is coming from renewable sources.

	CVD 1 (1 g)			CVD 1 (1 cm^2)		
	Commercial scale batch	Commercial scale continuous		Commercial scale batch	Commercial scale continuous	
Copper	203	203	Kg	0.016	0.016	g
Electricity	257	7.71	MJ	0.020	0.001	kJ
Hydrogen	37	37	kg	0.003	0.003	g
Argon	15896	477	kg	1.224	0.037	g
Hexane	27	27	kg	0.002	0.002	g

Table S10 – LCI of CVD graphene for commercial batch and commercial continuous scenario production for 1g OR 1cm^2 of graphene

Table S10 shows additional information on the commercial scale CVD process when using cm^2 instead of gram as functional unit. It also includes a variant of the process, called "continuous" that disregards ramp up and cooling time and considers only the resident time. This different approach reduces the electricity and the argon by roughly 95% while all other inputs remain unvaried as shown in Table S10.

	COMMERCIAL SCALE				DECARBONISED			
	CVD 1	KOH 15 V	rGO2C	rGO2T	CVD 1	KOH 15 V	rGO2C	rGO2T
Global Warming Potential [kg CO2-Equiv.]	5.7E+03	2.8E-01	8.1E-02	4.6E-02	5.7E+03	5.7E-02	7.9E-02	4.5E-02
Ozone Depletion [kg CFC 11-Equiv.]	6.0E-07	1.9E-10	9.5E-12	1.2E-11	5.8E-07	1.4E-11	8.3E-12	1.0E-11
Human toxicity, cancer [CTUh]	1.6E-05	2.4E-10	3.8E-10	2.9E-10	1.6E-05	3.8E-11	3.8E-10	2.9E-10
Human toxicity, non-canc. [CTUh]	4.6E-04	7.0E-09	3.0E-09	2.8E-09	4.6E-04	1.2E-09	3.0E-09	2.8E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	1.8E+00	8.8E-05	2.0E-05	2.2E-05	1.8E+00	4.8E-06	1.9E-05	2.2E-05
Ionising radiation, human health effect model, [kg U235 eq]	5.7E+02	8.7E-02	3.1E-02	2.3E-02	5.7E+02	3.6E-02	3.0E-02	2.3E-02
Photochemical ozone formation,[kg NMVOC]	8.3E+00	5.6E-04	1.5E-04	1.2E-04	8.3E+00	6.6E-05	1.5E-04	1.2E-04
Acidification [Mole of H+ eq.]	1.5E+01	1.5E-03	4.4E-04	4.8E-04	1.5E+01	1.1E-04	4.3E-04	4.7E-04
Terrestrial eutrophication, [Mole of N eq.]	3.1E+01	2.0E-03	4.6E-04	3.1E-04	3.1E+01	2.5E-04	4.5E-04	3.0E-04
Freshwater eutrophication, [kg P eq]	1.1E-02	4.6E-07	2.7E-07	1.5E-07	1.1E-02	1.7E-07	2.7E-07	1.5E-07
Ecotoxicity [CTUe]	3.1E+03	1.0E-02	8.8E-03	6.5E-03	3.1E+03	1.7E-03	8.8E-03	6.4E-03
Resources depletion, water [kg]	6.1E+01	2.9E-03	3.6E-04	2.6E-04	6.1E+01	1.0E-03	3.5E-04	2.5E-04
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	7.1E+00	4.4E-06	1.5E-06	2.0E-06	7.1E+00	3.8E-06	1.5E-06	2.0E-06

Table S11 – commercial scale and decarbonised scenarios for the production of 1 g of graphene: all impact categories

When looking at the LCA for all impact categories considering grams as functional unit, for both the commercial scale and decarbonised scenario (Table S11), it is clear how the CVD is the most impacting process while the chemical routes are the least impacting when scaled up. If considering the decarbonised scenario, instead, the electrochemical exfoliation becomes the least impacting in 7 categories out of 13 making it the most interesting material from an environmental perspective.

This study showed a comparative LCA for graphene production for 13 impacts categories and proved how the chemical processes (for GO2) are the least impacting for the environment and human health for all scenarios. When considering the laboratory processes, the rGO2T material is less impacting than the lowest impact electrochemically exfoliated material (KOH 15 V) with percentages ranging from a

33% in the ecotoxicity to an 82% in the ionising radiation. The rGO2C is 8% less problematic than the same exfoliated material in ecotoxicity and 80% for ozone depletion. From the resources depletion perspective, the best processes are also the chemical ones, and this is due to their better material conversion from graphite to graphene, as graphite production is the main cause of impact for this category. During the electrochemical exfoliation, the graphite used as binder in the rods (up to 70% according to the graphite rods producer) is lost in the solution and as CO_2.

When considering the commercial scale scenario, the chemical processes are still the least impacting in all categories, with percentages for the rGO2C ranging from 13% for ecotoxicity (36% for rGO2T) to 95% for ozone depletion (94% for rGO2T), and with the exception of the human toxicity (non-cancer) in which the exfoliation performs 36% better than rGO2C and 17% better than rGO2T.

The decarbonised scenario, shows how the electrochemical exfoliation process could improve its environmental performance using electricity generated by renewable sources. If so, this process could become better than the chemical ones in 7 out of 13 impact categories. However, the decarbonisation does not affect all background processes (i.e. all productions of input materials) due to data aggregation in GaBi. This also means that further studies are needed to understand if the chemical processes have the potential to remain the least impacting processes when all inputs are decarbonised.

	COMMERCIAL SCALE BATCH		COMMERCIAL SCALE CONTINUOUS	
	1g CVD 1	1cm^2 CVD 1	1g CVD 1	1cm^2 CVD 1
Global Warming Potential [kg CO2-Equiv.]	5.7E+03	4.4E-04	1.0E+03	7.9E-05
Ozone Depletion [kg CFC 11-Equiv.]	6.0E-07	4.7E-14	1.2E-07	8.9E-15
Human toxicity. cancer [CTUh]	1.6E-05	1.2E-12	1.3E-05	9.8E-13
Human toxicity. non-canc. [CTUh]	4.6E-04	3.5E-11	3.4E-04	2.6E-11
Particulate matter/Respiratory inorganics. [kg PM2.5-Equiv.]	1.8E+00	1.4E-07	1.3E+00	1.0E-07
Ionising radiation. human health effect model. [kg U235 eq]	5.7E+02	4.4E-05	4.6E+01	3.5E-06
Photochemical ozone formation.[kg NMVOC]	8.3E+00	6.4E-07	2.6E+00	2.0E-07
Acidification [Mole of H+ eq.]	1.5E+01	1.2E-06	5.7E+00	4.4E-07
Terrestrial eutrophication. [Mole of N eq.]	3.1E+01	2.4E-06	9.1E+00	7.0E-07
Freshwater eutrophication. [kg P eq]	1.1E-02	8.7E-10	2.2E-03	1.7E-10
Ecotoxicity [CTUe]	3.1E+03	2.4E-04	6.9E+03	5.3E-04
Resources depletion. water [kg]	6.1E+01	4.7E-06	9.8E+00	7.6E-07
Resource Depletion. fossil and mineral [kg Sb-Equiv.]	7.1E+00	5.5E-07	7.1E+00	5.5E-07

Table S12 – Additional information on CVD commercial scale production batch and commercial scale continuous production for 1g OR 1 cm²

Table S12 shows all impact categories for the commercial scale production of CVD 1 for both functional units (grams and centimetres squared) and for both process types (batch or continuous).

S 3 Comparison with previous studies

Comparing this study with previous research requires a different approach as all previous studies have not used the ILCD EU standard methodology and therefore different impact categories must be

introduced. All previous studies have considered the energy requirements for graphene production in MJ/kg (or kJ/cm^2) hence energy will be used as base for comparison.

	Energy use	
Pizza et al. (2014)	1.88	MJ/g
Arvidsson et al. (2014)		
Hummers	1.10	MJ/g
Hummers +	0.98	MJ/g
Hummers ++	0.87	MJ/g
Arvidsson et al. (2015)		
CVD min	6.6	kJ/cm^2
CVD base	22	kJ/cm^2
CVD Max	160	kJ/cm^2
Arvidsson et al. (2016)	**PED**	
Lab best case	11	MJ/cm^2
Lab worst case	79	MJ/cm^2
Pilot best case	11	MJ/cm^2
Pilot worst case	79	MJ/cm^2
Industrial best case	1.6	MJ/cm^2
Industrial worst case	79	MJ/cm^2

Table S13 – Summary table for other graphene studies

Pizza et al. (2014) propose an LCA of graphene as polymer filler, but not much is said about graphene alone, except that their production route (different from what we analyse, a mix of sulphuric and nitric acid at ambient temperature, microwave and milling) requires 1.88 MJ/g (Table S13) of primary energy. Arvidsson et al. (2014) proposes a hummers method using different quantities of solvent and oxidising agent and a different temperature and their result (1.10 MJ/g – Table S13) is comparable to our commercial scale simulation (1.64 MJ/g GCV – lab scale 3.29 MJ/g GCV). When considering their other 2 scenarios (Hummers+ and Hummers++), their results are still comparable, but they show values that are nearly half of what we found. It can be considered a minor difference since the recipes are slightly different and our study includes inputs production processes from GaBi dataset while theirs is based on the 1 to 3 conversion from electricity to heat input. The optimised lab scenario in our study shows higher PED due to the inevitably occurring heat losses of a hot plate.

Comparing the CVD studies is slightly more difficult as the two studies from Arvidsson et al. (2015 and 2016) assume a continuous process without ramp-up and cool down. In detail, Arvidsson et al. (2015) present range of results for CVD production of graphene that can be considered similar to our findings (batch lab scale 199 kJ/cm^2 GCV commercial scale 8.3 kJ/cm^2 GCV; continuous lab scale 7.4 kJ/cm^2 GCV commercial scale 1.7 kJ/cm^2 GCV) and ranging from a best-case scenario of 6.6 kJ/cm^2 to a worst case in the range of 160 kJ/cm^2. This is in line with our lab batch scenario, despite theirs being a continuous process. This is most likely due to differences in the carbon source gas (methane in Arvidsson et al. (2015); hexane in current study), its flow rate (from 35 to 350 cm^3/min in Arvidsson et al. (2015); 5 cm^3/min in current study) and residence time (1 and 10 minutes in Arvidsson et al. (2015); 5 minutes in current study). These differences make the continuous process analysed in Arvidsson et al. (2015) similar to our batch process as methane is by far their largest source of GWP. In our study, for the batch process the main contributors to the commercial scale CVD production are argon and copper, while for the continuous CVD production is the copper substrate as argon is used only to vent the furnace for a limited time prior to the release of the precursor gas.

In Arvidsson et al. (2016) the epitaxial growth of graphene is studied but, as they also state, this process requires 80 times greater energy input than CVD, mostly to produce the substrate (a SiC wafer). Compared with results of the current study, epitaxial graphene is associated with PED that is 3 orders of magnitude greater than our CVD results.