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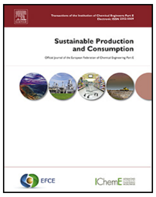

Research article

Environmental performance of different sorbents used for direct air capture

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ABSTRACT

Currently, conventional carbon dioxide (CO_2) mitigation solutions may be insufficient to achieve the stringent environmental targets set for the coming decades. CO_2 removal (CDR) technologies, such as direct air capture (DAC), capturing CO_2 from the ambient air, are required.

In this research, an independent life cycle assessment (LCA) of DAC adsorption systems based on three physisorbents (metal organic frameworks) and two chemisorbents (amine functionalized sorbents) is presented. These capture processes have been optimised by us in previous work.

Results show that for the overall capture process, negative CO_2 emissions are ensured by using a cellulose-based amine sorbent (cradle-to-gate) ensuring even the net removal of CO_2 from the atmosphere (cradle-to-grave). Processes using physisorbents have poorer performances. Chemisorbents yield operating conditions allowing lower impacts on the environment. In 2050, these processes could reduce climate change but can generate other environmental impacts.

With the aim to have better environmental performances of DAC systems, future research should be focused on improving the physical properties of sorbents such as the silica gel based amine sorbent to increase their capture capacities. If metal organic frameworks are to be used, it is necessary to drop their energy consumption (by increasing the loading) and the required mass of sorbent.

1. Introduction

Carbon dioxide (CO_2) emissions are rising in the world, with the increase of energy demand and industrial development, reaching a value of 36.44 billion tonnes in 2019 (World Data, 2021). Consequently, the global CO_2 concentration has risen at an average rate of 2.4 ppm/year in the last decade, assuming a value of 414 ppm in 2019 (Jeong-Potter and Ferrauto, 2021). High CO_2 concentrations cause climate change, and urgent solutions are needed to keep the increase of temperature to below 1.5 °C above the pre-industrial level by the end of the century. However, to reach this objective, conventional mitigation solutions based on the reduction of CO_2 emissions are not enough, and CO_2 removal is needed through Negative Emission Technologies (NETs) or Carbon Dioxide Removal (CDR) (Lackner, 2015). Afforestation, bioenergy with carbon capture and storage, ocean fertilization, biochar, enhanced weathering and direct air capture (DAC) are possible options for CDR (Fuss et al., 2014). DAC has several advantages regarding water and land uses, plant location, technology readiness level (TRL), and that CO_2 capture from the atmosphere allows disperse sources (representing about 50% of total emissions) to also be tackled (Terlouw et al., 2021a, 2021b). CO_2 captured by DAC could subsequently be permanently geologically sequestered, thus removing it from the air in the long term, similar to a CDR technology, but some have suggested that the captured CO_2 could be used in chemical processes in the short term too (Bos et al., 2020; Kar et al., 2018).

The DAC strategy can be based on several technologies such as absorption, adsorption, membrane and mineral carbonation, and it has been reviewed in the literature by Sanz-Pérez et al. (2016), Shi et al. (2020) and Kelemen et al. (2020). Moreover, photocatalysis technology has been discussed by Adamu et al. (2020) and cryogenic separation by von Hippel (2018). Other technologies such as an electrochemical approach or electrodialysis have been proposed in Eisaman et al. (2009) and Sabatino et al. (2020), respectively.

Currently, absorption and adsorption are the most mature and investigated technologies in the literature. These two processes are based on two steps. Firstly, the CO_2 is captured by using an air contactor, and secondly the solvent (aqueous alkaline solutions) or solid sorbent (solid alkali carbonates sorbents, amine functionalized sorbents, metal organic frameworks (MOFs), zeolites) is regenerated (Sanz-Pérez et al., 2016). The adsorption option uses a simpler

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regeneration process, potentially exploiting low grade heat, that could be waste or renewable (70–100 °C) (Realmonte, 2017).

The first commercial DAC system is based on adsorption and it was realized by the Climeworks company, in Switzerland (Hinwil) (Vito, 2020). The company has other pilot plants in Iceland (Hellisheidi) for the removal of CO_2, which is subsequently stored underground for mineralization, in Italy (Troia), where CO_2 is used to produce methane and in Germany (Dresden), where the captured CO_2 is used to produce fuels (Climeworks, 2020a). Other companies such as Global Thermostat, Antecy, Hydrocell, Skytree use adsorption technology to capture CO_2 from the air (Fasihi et al., 2019). Only Carbon Engineering, with a demonstration plant in Canada (Squamish), utilizes a technology based on absorption (Keith et al., 2018).

Performances of DAC processes are evaluated and compared by using Key Performance Indicators (KPIs) such as: operating costs (OPEX), capital costs (CAPEX), thermal and electrical energy consumptions, TRL, autonomy, scalability, potential for intermittent operation, minimum and maximum operating temperature, requirements for cooling, air purification requirements, degradation of sorbent, physical robustness, environmental impact, land use and water demand. The OPEX, CAPEX, total costs, thermal and electrical energy consumptions are most discussed in the existing literature: a wide range for their values has been determined, especially for costs (Fasihi et al., 2019).

Fuss et al. (2018) have estimated DAC costs up to 1000 \$/tonne CO_2, which they state could decrease to 100–300 \$/tonne CO_2 by 2050. House et al. (2011) have suggested a range of 35–1000 \$/tonne CO_2. We consider that costs evaluated by DAC companies are frequently optimistic, and require independent verification, as has been attempted in Leonzio et al. (2022). In this study it was found that Climeworks has claimed a somewhat lower cost (600 \$/tonne CO_2) compared to that obtained by authors with more strict assumptions (962 \$/tonne CO_2).

Regarding the energy consumption, for the absorption process, the required thermal energy has been estimated to be in the range of 1420–2450 kWh_{th}/tonne CO_2 (Zeman, 2007; Keith et al., 2018), while the electrical energy consumption has been evaluated to be in the range of 366–2790 kWh_{el}/tonne CO_2 (Baciocchi et al., 2006; Li et al., 2015; Keith et al., 2018). It has been suggested that for the DAC adsorption system, the thermal energy requirement can be estimated to be between 1400 and 2000 kWh_{th}/tonne CO_2 (Kulkarni and Sholl, 2012; Vito, 2020; Fasihi et al., 2019), while electricity consumption ranges between 218 and 1420 kWh_{el}/tonne CO_2 respectively (Sinha et al., 2017; Fasihi et al., 2019; Vito, 2020).

Some literature in the public domain has investigated the land use impact associated with DAC and some results have been reported. The land use impact results for Carbon Engineering, Climeworks and Global Thermostat is >0.016 km^2/(mtonne CO_2year), 0.1 km^2/(mtonne CO_2year) and 0.05–0.002 km^2/(mtonne CO_2year) respectively (Viebahn et al., 2019).

For DAC absorption processes such as that of Carbon Engineering, water is normally lost during the operation, as the moisture present before calcination in a kiln must be removed. 0–50 tonnes of water is lost per tonne of captured CO_2; this depends on factors such as humidity and air temperature (Broehm et al., 2015). It has been reported that using the technology of the Carbon Engineering, 4.7 tonnes of water/tonne CO_2 captured are lost (Vito, 2020). On the other hand, with DAC adsorption processes, water is produced as a by-product: 0.8–2 tonnes of water/tonne CO_2 captured are produced by Climeworks (Vito, 2020).

There is very little information on DAC technology in the literature related to its environmental impact. It is important to evaluate the environmental burden of these emerging processes, in a transparent and consistent way, due to the important role that these systems may have in the near future (Terlouw et al., 2021a, 2021b). While DAC removes CO_2 from the atmosphere, it still requires energy and materials use. Therefore, it is fundamental to evaluate the net CO_2 removal for the overall process, using a life cycle assessment (LCA) methodology (Deutz and Bardow, 2021).

There are a very limited number of studies about the LCA of DAC systems in the literature. An LCA of a DAC adsorption process was conducted by Deutz and Bardow (2021) and Terlouw et al. (2021a, 2021b). Liu et al. (2020) and de Jonge et al. (2019) also conducted an LCA study of DAC absorption system. van der Giesen et al. (2017) analyzed the environmental burden of a DAC ion exchange resin.

The first study aiming at the evaluation of the environmental impact of a DAC absorption process was conducted by de Jonge et al. (2019). Here, they examined the full system from capture to storage, suggesting hot-spots for CO_2 emissions, alongside evaluating the relative net amount of CO_2 captured by the system (life cycle carbon efficiency). Results show that a carbon efficiency of 62% can be ensured, while hotspots throughout the entire system are related to energy production (electrical and thermal energies). This suggests that the use of renewable energies could help lower the environmental impact.

In Liu et al. (2020), the first cradle to grave LCA of a DAC-to-fuel process was carried out (from raw material to end use and disposal). The DAC plant was paired with a Fischer-Tropsch synthesis process, producing diesel for transportation from the captured CO_2. Results show that the process could produce diesel fuel with a carbon intensity lower than that of the conventional process, at 29 gCO_{2eq}/MJ, compared to 75 gCO_{2eq}/MJ from traditional fuel. These data were produced considering an electricity emission factor lower than 139 gCO_{2eq}/kWh, suggesting that this plant should be located in regions with very low grid emission factor or powered by a renewable source of electricity.

van der Giesen et al. (2017) performed an LCA for a DAC ion exchange resin and compared it to a traditional monoethanolamine (MEA) based post-combustion capture (PCC) system. The PCC system could reduce climate change impact by 73%, from 0.85 to 0.23 $kgCO_{2eq}$/kWh. Results show that in order to achieve the same greenhouse gas (GHG) reduction, the DAC system had worse impacts in nine other categories, if electricity from coal was used. This was attributed to a higher electricity demand per amount of captured CO_2, when capturing CO_2 from the air.

Another important DAC process considered for an environmental analysis is adsorption. In the work of Deutz and Bardow (2021), an LCA for Climeworks plants in Switzerland (Hinwil) and Iceland (Hellisheidi) was conducted. Results show that both plants, when storing the captured CO_2, can achieve negative CO_2 emissions, with a carbon capture efficiency of 84.5% and 93.1%, respectively. The environmental impact is strongly influenced by energy supply (electricity and heat). However, with low carbon energy, sorbent and infrastructure have significant effects on the environmental impact. The authors considered six amine functionalized sorbents and they found that to capture 1% of the global annual CO_2 emissions in 2019, 3683 DAC plants with a capacity of 100,000 tCO_2/year per plant are required.

Another environmental analysis for the DAC adsorption system based on that of Climeworks has been reported in the work of Terlouw et al. (2021a). A cradle to grave study was developed, considering different electricity (grid and photovoltaic) and heat (electricity for heat pump, waste and solar energy) sources, in several countries. Results show that net negative CO_2 emissions are ensured for all of the investigated systems in all countries, with the best performances (96% of GHG removal efficiency) for the system located in Norway using waste heat, and electricity from the grid.

The two previous research studies about the adsorption process were based on proxy data for sorbents and considered the same amount of sorbent in different case studies, with limited level of transparency. This in itself does not ensure an accurate LCA. Moreover, Terlouw et al. (2021b) argued for transparency and suggested to consider a detailed inventory of CDR technologies (and DAC), such as sorbents. It is for this reason that in this research, an LCA study was conducted for DAC adsorption systems, following the procedure described in Leonzio et al. (2022) using actual data for sorbents and their syntheses obtained from the literature. These DAC adsorption processes are based on the Climeworks plant and different sorbents: two amine functionalized sorbents, SI-AEATPMS ([N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane (AEATPMS) grafted on silica gel) and APDES-NFC-FD (3-aminopropylmethyldiethoxysilane (APDES) on nanofibrillated cellulose (NFC)), and three MOFs (MIL-101, MOF-177, MOF-5). Moreover, as an additional point of novelty, we carried out an environmental analysis of DAC processes using MOFs, for which only a few LCA analyses have been reported in the literature, in particular regarding its production (MOF-74 has been considered in Grande et al. (2017), while UiO-66-NH_2 was discussed in Luo et al. (2021)).

In this work, SI-AEATPMS and APDES-NFC-FD were considered because suggested by the Climeworks company for DAC systems. On the other hand, MOFs were taken into account because these show good performances at high CO_2 concentration. Our aim was to verify the performance of MOFs at low CO_2 concentration, such as that within ambient air (Elhenawy et al., 2020).

2. Materials and methods

LCA is a quantitative methodology used to evaluate the environmental impact of a product or service according to the International Organization for Standardisation (ISO) standards 14040 and 14044 (ISO 14040, 2009; ISO 14044, 2006). Four important phases characterize this analysis: goal and scope definition, life cycle inventory (LCI), life cycle impact assessment (LCIA) and interpretation (ISO 14040, 2009; ISO 14044, 2006). To develop the LCA, the software SimaPro was used with an attributional approach. The above LCA phases are analyzed in this section, after a brief description of the investigated DAC adsorption processes.

2.1. Process description

DAC processes were presented in Leonzio et al. (2022), considering the geometry of a single adsorbent module defined by Climeworks (area footprint excl. options of 20 m^2, with a length of 3.2 m) and an air flow rate of 2.86 m^3/s (Climeworks, 2020b). While we considered only 1 adsorbent bed, the company has a plant with 18 adsorbent unit beds, 3 rows of beds with 6 unit beds each. The air contactor was studied for chemisorbents such as amine functionalized sorbents (APDES-NFC-FD and SI-AEATPMS) and some physisorbents such as metal organic frameworks (MOF-177, MOF-5, MIL-101). The cellulose based amine functionalized sorbent was used by Climeworks within its plant. CO_2 was captured from the dried air (we are supposing that water, as humidity, is removed before the adsorption), having a CO_2 concentration of 400 ppm, by the sorbent bed and it was released by a variation of temperature, as a temperature swing adsorption (TSA) process (the adsorption temperature was set at 298 K, while the regeneration temperature was 373 K). Cooling water was used for the cooling step, while electricity for fans and heat for the regeneration step were provided by a municipal waste incinerator (MWI), as in the Climeworks plant.

2.2. Goal and scope of the study

The main aim of this study was to evaluate the environmental performance of adsorption systems capturing CO_2 from the air with different sorbents (physisorbents as MOF-177, MIL-101, MOF-5 and chemisorbents as APDES-NFC-FD, SI-AEATPMS). These processes were designed before in Leonzio et al. (2022) as described in Section 2.1. It was also necessary to evaluate the environmental impact of synthesis routes for amine functionalized sorbents and MOFs appropriate for DAC systems.

2.2.1. Functional unit

The aim of a DAC system is to capture CO_2 from the atmosphere. In view of this, the LCA was developed considering 1 tonne of CO_2 captured as the functional unit, providing a reference to which all inputs and outputs related to the DAC processes can be compared and discussed (Terlouw et al., 2021b).

2.2.2. System boundaries

Putting the attention on the environmental performance of this new emerging technology using different sorbents, we conducted a cradle-to-gate analysis. This means that the use of the captured CO_2 (whether permanently stored or re-used in other chemical processes) was not considered during the evaluation of the environmental burden, but only processes up to the delivery of the captured CO_2. System boundaries, describing which processes were included in the assessment are shown in Fig. 1.

Here, all processes that were considered for the analysis are within the red line (system boundaries) and are the following: the MWI producing electrical and thermal energies, sorbent production process and its disposal (by using an anion exchange resin for amine functionalized sorbents (Deutz and Bardow, 2021) and an incinerator for MOFs (Nanoshell, 2021)) and DAC plant (including adsorption, desorption and cooling stages). The air and water were taken from nature and were considered to be outside the system boundaries, alongside emissions and water discharged into nature. As a cradle-to-gate analysis, the use of storage or utilization of the captured CO_2 was also considered as being outside the system boundaries.

2.3. Life cycle inventory phase

In the LCI phase, all inputs and outputs (material and energy balances) for the DAC processes were provided based on 1 tonne CO_2 captured as a functional unit, utilizing the results of the DAC design presented in Leonzio et al. (2022). Moreover, the synthesis routes of all sorbents were based on mass assumptions only and therefore underestimate the correct environmental impacts, due to the lack of data in the existing literature. This point should be improved in the future research.

2.3.1. Life cycle inventory phase for sorbent syntheses

The synthesis of APDES-NFC-FD and SI-AEATPMS sorbents has been reported in Wurzbacher (2015). The former sorbent has been synthesized by adding the amine APDES to NFC hydrogel (concentrated from 0.5% w/w to 8.46% w/w by centrifugation), forming a suspension with an amine concentration of 10% w/w, after a 2 hour incubation period. The obtained compound was dropped into liquid N_2, freeze-dried for 48 h, and subjected to a thermal treatment at 393 K by using a natural convection oven for 2 h. The amine content, reported as the nitrogen content, was 3.86 $mmol_N/g_{sorbent}$ (Wurzbacher, 2015). Table 1 shows the main material inputs for the production of this amine functionalized sorbent (Wurzbacher, 2015).

The synthesis of the amine APDES has been presented by Kleinstick (1977), as reported in the Supplementary information through Tables SI 1–SI 6. The production of NFC through an alkaline pretreatment route has been suggested by Lee (2016) and reported in Table SI 7 of the Supplementary information.

The SI-AEATPMS sorbent has been obtained by loading the amine AEATPMS (11.12 g) onto silica gel (20 g), dried in a natural convection oven at 383 K. The obtained compound was heated at 423 K in a silicone oil bath for 3 h and after that, it was cooled to 298 K, washed and dried in the ambient air for 24 h (Wurzbacher, 2015). The amine content of SI-AEATPMS was 2.48 $mmol_N/g_{sorbent}$ (Wurzbacher, 2015). Table 2 shows the main material inputs for the synthesis of this sorbent (Wurzbacher, 2015).

The amine AEATPMS synthesis was proposed in the work of Uehara et al. (1995) and is reported in the Supplementary information of this work, with the main material inputs for the production of each reactant in Tables SI 8–SI 11. For the silica gel production, data provided by the Idemat database and present in SimaPro was used (Idemat, 2001).

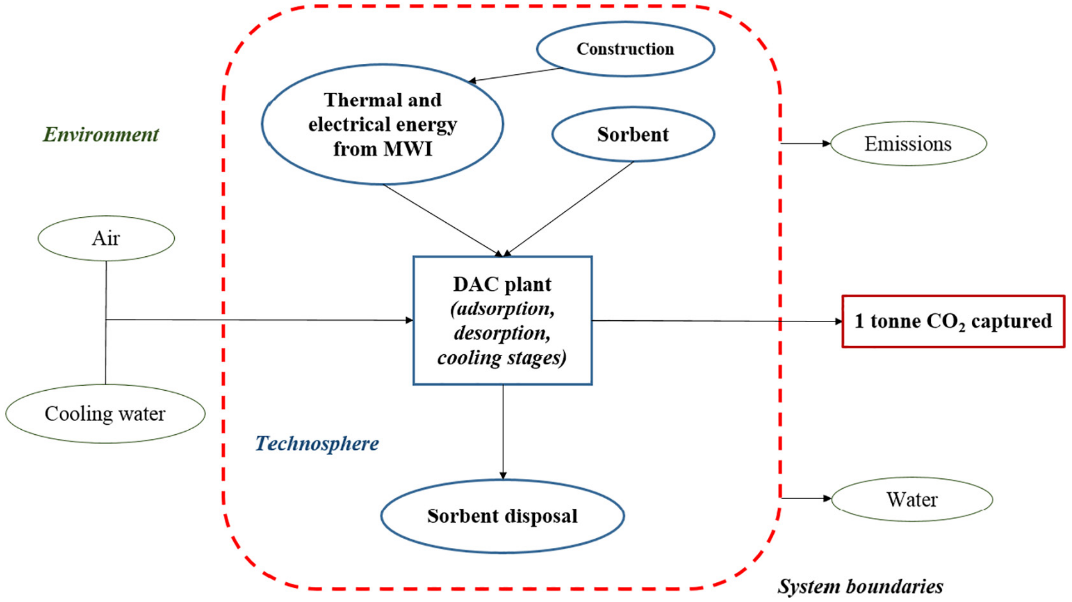

Fig. 1. System boundaries of DAC adsorption systems (DAC=direct air capture, MWI = municipal waste incinerator).

Different synthesis routes have been suggested for MOFs. In the work of Peedikakkal et al. (2020) the production of MOF-5 has been reported. MOF-5 was prepared by mixing zinc nitrate hexahydrate (340 mg), 1,4-benzenedicarboxylic acid (127 mg) and *N*,*N*-dimethylformamide (20 mL) in a glass vial. The mixture was sonicated for 5 min and heated in an oven at 373 K for 24 h, producing some colourless and cubic crystals. After that, the solution was cooled to room temperature and the mother liquor was decanted from the crystalline material. The white solid was washed with 50 mL of dimethylformamide, filtrated and washed again. 350 mg of MOF-5 were obtained. Table 3 shows the main material inputs for the production of 1 kg of MOF-5. In the Supplementary information (Table SI 12) the main material inputs for the zinc nitrate hexahydrate synthesis are reported, while the data for the other two reagents were taken from the Ecoinvent database (Ecoinvent, 2018).

The production of MOF-177 has been reported in Tranchemontagne et al. (2008). Benzenetribenzoic acid (626 mg) and zinc acetate dihydrate (2.51 g) were mixed in 50 mL of diethylformamide for 3 h. The mixture was filtrated, washed with 10 mL of diethylformamide, immersed in 40 mL of trichloromethane and refreshed several times in 5 days. The solution was decanted and the product was split into two samples, one for the bulk activation and one for the activation in a quartz cell for N_2 sorption. Both samples were activated under vacuum at 393 K for 12 h, giving 490 mg of MOF-177 (reaction yield of 60%). Table 4 shows the main material inputs for the production of 1 kg of MOF-177.

Tables SI 13–SI 18 of the Supplementary information report the main material inputs for the production of reagents not present in the SimaPro database.

Férey et al. (2005) described in their work the synthesis of MIL-101. Chromium nitrate nonahydrate (400 mg), fluorhydric acid (20 mg), 1,4-benzene dicarboxylic acid (164 mg) and water (4.8 mL) were mixed and heated to 493 K for 8 h. After natural cooling, the mixture was filtered, producing 302 mg of MIL-101 (reaction yield of 50%). Table 5 shows the main material inputs for this synthesis route. In the Supplementary information, Tables SI 19–SI 20 present the main material inputs for the production of reactants involved in the MIL-101 synthesis, not present in the SimaPro database.

As at the industrial level, we considered the recycling of solvent to be 99% in the MOF-5 and MOF-177 syntheses.

2.3.2. Life cycle inventory phase for DAC systems

Table 6 shows the inventory data for DAC adsorption systems to capture 1 tonne of CO_2. The amount of sorbent, air, electrical and thermal energies, cooling water and waste for the MWI producing the required energy output were all considered as inputs. With the exception of the process using the amine cellulose based sorbent, the adsorbent beds used a high amount of sorbent per tonne of captured CO_2: the highest value is for the system using MOF-5 with 186 $kg_{sorbent}$/tonne CO_2 captured, against the process using APDES-NFC-FD for which 7 $kg_{sorbent}$/tonne CO_2 captured were needed. Regarding the air consumption, the systems using MOFs are characterized by higher values (the highest value is for the process using MIL-101 where 3116 tonne of air were required to capture 1 tonne of CO_2), due to a lower CO_2 adsorption flow rate.

Electrical and thermal energies and cooling water consumptions were discussed before: the MOF adsorbent beds are characterized by higher consumptions due to a lower working capacity (the difference

Table 1
Main material inputs for the production of 1 kg of APDES-NFC-FD (Wurzbacher, 2015) (APDES = 3-aminopropylmethyldiethoxysilane, NFC = nanofibrillated cellulose).

Inputs		
APDES	0.739	kg
Water	117	kg
NFC	0.586	kg
Outputs		
APDES-NFC-FD	1	kg

Table 2
Main material inputs for the production of 1 kg of SI-AEATPMS (Wurzbacher, 2015) (SI=silica gel, AEATPMS = [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane).

Inputs		
Silica gel	0.496	kg
AEATPMS	0.276	kg
Outputs		
SI-AEATPMS	1	kg

Table 3
Main material inputs for the production of 1 kg of MOF-5 (Peedikakkal et al., 2020).

Inputs		
Zinc nitrate hexahydrate	0.971	kg
1,4-Benzenedicarboxylic acid	0.363	kg
N,*N*-dimethylformamide	350	kg
Outputs		
MOF-5	1	kg

Table 5
Main material inputs for the production of 1 kg of MIL-101 (Férey et al., 2005).

Inputs		
Chromium nitrate nonahydrate	1.323	kg
Fluorhydric acid	0.066	kg
1,4-Benzene dicarboxylic acid	0.542	kg
Water	15.871	kg
Outputs		
MIL-101	1	kg

between the loading at the end of adsorption and desorption stage) (Leonzio et al., 2022). Electricity for fans and heat for regeneration were supplied by a MWI. The LCA considered the MWI to be within the system boundary, alongside the amount of wastes needed as feedstock to generate the required energy requirement.

In the work of Hellweg et al. (2001) it was reported that 4.5 MJ of heat is produced per kg of waste, while 2.2 MJ of electricity is generated per kg of waste. The adsorption system using MOF-177 has a high demand for thermal energy, hence a high amount of waste input requirement (1037 $\text{tonnes}_{\text{waste}}$/tonne CO_2 captured).

Generally, MWI generates three products/service: electricity, heat (as by-products as intermediate flows) and waste treatment. An allocation factor based on energy was used for the heat and power production respectively of 67.2% and 32.8% (Hellweg et al., 2001).

In our calculation, we neglected the energy for pumping the cooling water: from Aspen Plus we found that 0.029 kWh/m^3 of cooling water are needed, that corresponds to about 1% of the overall Cumulative Energy Demand (CED) of each process.

2.4. Life cycle impact assessment methodology

The environmental impacts were evaluated through two different steps of the LCIA phase: classification and characterization. The LCI results were generated and organized into impact categories and then into impact indicators at the midpoint level using the Environmental Footprint 2.0 method, recommended by the European Commission's Joint Research Centre (European Commission, 2018) using SimaPro. In addition to climate change, other different midpoint impact categories were considered to determine potential environmental trade-offs: ozone depletion, ionizing radiation, photochemical ozone formation, respiratory inorganics, non cancer human health effect, cancer human health effect, acidification terrestrial and freshwater, eutrophication freshwater, eutrophication marine, eutrophication terrestrial, ecotoxicity freshwater, land use, water scarcity, resource use, energy carriers and resource use, mineral and metal.

3. Results and discussion

3.1. Results for sorbent production

Results for the environmental analysis of processes producing 1 kg of sorbent are reported in Table 7 with Sankey diagrams in Figs. SI 1–SI 5 of the Supplementary information. It is evident that regarding climate change impact, the SI-AEATPMS production has the lowest value (4.12 $kgCO_{2eq}/kg_{sorbent}$) impact, while the MOF-177 synthesis has the highest impact (49.1 $kgCO_{2eq}/kg_{sorbent}$). Fig. 2 shows the contribution of each input to the overall climate change impact of sorbent production process, for all considered sorbents. The contribution is reported as a percentage of the total climate change value, as reported in the x-axis.

Table 4
Main material inputs for the production of 1 kg of MOF-177 (Tranchemontagne et al., 2008).

Inputs		
Benzenetribenzoic acid	1.278	kg
Zinc acetate dihydrate	5.143	kg
N,N-diethylformamide	110.20	kg
Trichloromethane	121.79	kg
Outputs		
MOF-177	1	kg

The production of AEATPMS has a high climate change impact of 84.2% (3.47 $kgCO_{2eq}/kg_{sorbent}$), while the silica gel production is less significant for this impact category. For the other amine functionalized sorbent, for which climate change impact has a value of 26.2 $kgCO_{2eq}/kg_{sorbent}$, the cellulose production has the highest impact (50.4%) on this impact category, even though the amine synthesis has a great contribution (49.2%). The significant impact of the amine synthesis on climate change suggests that future research should be focused on alternative production routes that can potentially offer lower CO_{2eq} emissions. Moreover the use of NFC as support is not suggested while a more environmental friendly one is advised.

For the MIL-101 sorbent, the synthesis of chromium nitrate nonahydrate contributes 80.3% of the overall climate change impact, followed by the 1,4-benzene dicarboxylic acid synthesis (19.4%). As a significant factor, by using a lower amount of chromium nitrate nonahydrate could reduce the environmental impact of MIL-101 production.

The other reagents are not so significant for the overall CO_{2eq} emissions, which are 5.41 $kgCO_{2eq}$ per kg of sorbent. This last value is the lowest among the other MOFs due to the use of water in synthesis.

Less environmental friendly solvents were used in the synthesis of the other two MOFs. Evidently, future research should suggest new synthesis routes that avoid the utilization of organic solvents in order to potentially lower the climate change impact (Grande et al., 2017).

The benzenetribenzoic acid and zinc acetate dihydrate utilization in the production of MOF-177 has a higher influence on the total climate change impact of 54.2% and 24.4% respectively.

With respect to MOF-5, the *N*,*N*-dimethylformamide synthesis contributes 69.3% of the total CO_{2eq} emissions of 9.14 $kgCO_{2eq}/kg_{sorbent}$, then reducing its amount in this synthesis is suggested in order to have a lower significant impact. These considerations are valid for MOF-177 synthesis too, where N,N-diethylformamide and trichloromethane are significant.

Results for all investigated sorbents show that climate change impact values are in agreement with those reported in the literature, particularly in the work of Deutz and Bardow (2021) for amine functionalized sorbents and in the work of Grande et al. (2017) for MOFs. In these studies, a wide range (1136.2–12.3 $kgCO_{2eq}/kg_{sorbent}$) of climate change impact was suggested depending on the synthesis method used.

Considering other impact categories and the results for the production of 1 kg of SI-AEATPMS and MIL-101 we have that although the silica gel based sorbent has a lower environmental impact on climate change, the production of MIL-101 has lower values for ozone depletion, ionization radiation, non-cancer human health effect, euthrophication freshwater, euthrophication marine, land use, water scarcity and resource use, energy carriers. On the other hand, comparing the results for the production of 1 kg of SI-AEATPMS with that of MOF-177 and MOF-5

Table 6

Inventory data for DAC adsorption processes capturing 1 tonne of CO_2 (SI=silica gel, AEATPMS = [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane, APDES = 3-aminopropylmethyldiethoxysilane, NFC = nanofibrillated cellulose) (Leonzio et al., 2022).

Sorbent	MIL-101	MOF-177	MOF-5	APDES-NFC-FD	SI-AEATPMS
Inputs					
Sorbent mass (kg/tonne CO_2)	173	120	186	7	129
Air (tonne/tonne CO_2)	3116	2735	3082	1851	1917
Electrical energy (kWh_{el}/tonne CO_2)	1388	1218	1373	270	322
Regeneration energy (kWh_{th}/tonne CO_2)	1,068,100	1,296,600	493,900	1428	1884
Waste for MWI (tonne/tonne CO_2)	854	1037	395	1	2
Cooling water (m^3/tonne CO_2)	459,034	55,729	21,227	614	809
Outputs					
Captured CO_2 (tonne)	1	1	1	1	1

we have that the amine sorbent production has a lower burden in 15 out 16 impact categories and in 14 out 16 impact categories respectively. While the production of 1 kg of cellulose based amine sorbent causes an environmental burden slightly higher compared to that of silica gel-based amine sorbent in 15 out 16 impact categories, as well as in comparison with MOF-5 (in 15 out 16 impact categories) and MIL-101 (in 14 out 16 impact categories).

These studies highlight the need to shift the research concerning the synthesis of MOFs to routes based on aqueous solutions, especially when these will be implemented on a large scale, as also found by Grande et al. (2017) and Luo et al. (2021). Moreover, as the environmental impact of MIL-101 production is comparable with that of SI-AEATPMS, modifications are necessary to improve the loading, and increase the working capacity of this MOF in order to be used for CO_2 capture at low concentrations, such as those of CO_2 from the atmosphere and then in order to reduce energy consumptions for this aim. Keeping the same structure and synthesis, some materials (for example among amines) with a low environmental impact but with a high CO_2 adsorption capacity could be added to MIL-101 to improve its overall performances.

3.2. Results for DAC adsorption systems

Table 8 shows results for the LCIA of DAC adsorption processes capturing 1 tonne of CO_2, while Sankey diagrams are in Figs. SI 6–SI 10 of the Supplementary information. The DAC process using the cellulose-based amine sorbent is the only one in this study that ensures an overall negative CO_2 emissions factor of −116 $kgCO_{2eq}$/tonne CO_2 captured for the cradle-to-gate system (for the results and discussion of this work, we are referring to a negative climate change/CO_2 emissions if a negative value is obtained in the cradle-to-gate analysis, while a net negative climate change/CO_2 emissions if the removal of CO_2 is present in the cradle-to-grave analysis).

Although the silica gel-based amine sorbent produced for the DAC system that uses adsorption has the lowest environmental impact for climate change, it does not enable negative CO_2 emissions, with a value of 6.25×10^2 $kgCO_{2eq}$/tonne CO_2 captured. This is mainly due to the amount of the used sorbent that is greater compared to that of the DAC system using the other amine sorbent and that causes a significant footprint impact. The DAC process using MOF-177 as sorbent has the highest carbon emission of 5.3×10^5 $kgCO_{2eq}$/tonne CO_2 captured. Other systems using MOF-5 and MIL-101 have a climate change impact value of 2.01×10^5 $kgCO_{2eq}$/tonne CO_2 captured and 4.33×10^5 $kgCO_{2eq}$/tonne CO_2 captured respectively.

The contribution of each process to the overall climate change impact is illustrated in Table 9. Comparing data related to the DAC plant using the cellulose based amine and silica gel based amine sorbent, it is possible to verify that the large amount of the second sorbent (129 $kg_{sorbent}$/tonne CO_2 captured, as in Table 7) causes a significant positive value of the footprint for the sorbent production and disposal (699 $kgCO_{2eq}$/tonne CO_2 captured). On the other hand, for the former sorbent (cellulose based amine sorbent), 7 $kg_{sorbent}$/tonne CO_2 captured produces only 181 $kgCO_{2eq}$ per tonne of captured CO_2.

The difference of CO_2 emissions in the two sorbent productions/disposals is caused by the different sorbent adsorption capacity that is lower for SI-AEATPMS, so that a greater mass is required producing a higher environmental impact for its total production and disposal.

For the DAC system using SI-AEATPMS, a slightly higher energy consumption causes a slightly higher environmental impact compared to the DAC system based on APDES-NFC-FD. The cooling water is assumed not to have an impact, as it is taken directly from nature and we neglected the pumping energy. These considerations suggest that in order to improve the environmental impact of the DAC plant using SI-AEATPMS with the aim to have negative emissions, it is necessary to change the production/disposal stage of the same sorbent.

Table 7

LCIA results for the production of 1 kg of sorbent (SI=silica gel, AEATPMS = [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane, APDES = 3-aminopropylmethyldiethoxysilane, NFC = nanofibrillated cellulose).

Sorbent	MIL-101	MOF-177	MOF-5	APDES-NFC-FD	SI-AEATPMS
Climate change ($kgCO_{2eq}$)	5.42	$4.91 \cdot 10^{1}$	9.14	$2.62 \cdot 10^{1}$	4.12
Ozone depletion ($kgCFC_{11eq}$)	$3.28 \cdot 10^{-7}$	$8.89 \cdot 10^{-4}$	$1.38 \cdot 10^{-6}$	$8.28 \cdot 10^{-6}$	$2.03 \cdot 10^{-6}$
Ionizing radiation ($kBqU\text{-}235_{eq}$)	$4.61 \cdot 10^{-1}$	$1.13 \cdot 10^{1}$	2.24	7.22	1.51
Photochemical ozone formation ($kgNMVOC_{eq}$)	$1.3 \cdot 10^{-2}$	$1.34 \cdot 10^{-1}$	$2.08 \cdot 10^{-2}$	$7.07 \cdot 10^{-2}$	$1.1 \cdot 10^{-2}$
Respiratory inorganics (disease incidences)	$2.06 \cdot 10^{-7}$	$2.18 \cdot 10^{-6}$	$2.45 \cdot 10^{-7}$	$1.01 \cdot 10^{-6}$	$1.92 \cdot 10^{-7}$
Non cancer human health effect (CTUh)	$3.1 \cdot 10^{-7}$	$-1.58 \cdot 10^{-6}$	$2.28 \cdot 10^{-6}$	$2.44 \cdot 10^{-6}$	$1.09 \cdot 10^{-6}$
Cancer human health effect (CTUh)	$1.54 \cdot 10^{-5}$	$4.78 \cdot 10^{-7}$	$8.99 \cdot 10^{-8}$	$4.15 \cdot 10^{-7}$	$5.76 \cdot 10^{-8}$
Acidification terrestrial and freshwater ($molH^{+}_{eq}$)	$3.2 \cdot 10^{-2}$	$3.43 \cdot 10^{-1}$	$4.28 \cdot 10^{-2}$	$1.18 \cdot 10^{-1}$	$3.08 \cdot 10^{-2}$
Euthrophication freshwater (kgP_{eq})	$9.26 \cdot 10^{-4}$	$1.31 \cdot 10^{-2}$	$3.31 \cdot 10^{-3}$	$8.13 \cdot 10^{-3}$	$2.15 \cdot 10^{-3}$
Euthrophication marine (kgN_{eq})	$4.15 \cdot 10^{-3}$	$6.18 \cdot 10^{-2}$	$6.57 \cdot 10^{-1}$	$2.05 \cdot 10^{-2}$	$8.64 \cdot 10^{-3}$
Euthrophication terrestrial ($molN_{eq}$)	$6.83 \cdot 10^{-2}$	1.15	$9.73 \cdot 10^{-2}$	$2.11 \cdot 10^{-1}$	$4.14 \cdot 10^{-2}$
Ecotoxicity freshwater (CTUe)	$1.55 \cdot 10^{2}$	$6.99 \cdot 10^{1}$	6.22	$1.25 \cdot 10^{1}$	2.28
Land use (Pt)	5.68	$1.46 \cdot 10^{3}$	5.29	$4.46 \cdot 10^{1}$	$8.35 \cdot 10^{1}$
Water scarcity (m^3 depriv)	$3.15 \cdot 10^{2}$	$5.78 \cdot 10^{3}$	$1.06 \cdot 10^{3}$	$1.83 \cdot 10^{3}$	$6.81 \cdot 10^{2}$
Resource use, energy carriers (MJ)	$6.18 \cdot 10^{1}$	$8.48 \cdot 10^{2}$	$2.06 \cdot 10^{2}$	$5.08 \cdot 10^{2}$	$8.19 \cdot 10^{1}$
Resource use, mineral and metal ($kgSb_{eq}$)	$1.33 \cdot 10^{-4}$	$1.08 \cdot 10^{-4}$	$3.04 \cdot 10^{-5}$	$1.41 \cdot 10^{-4}$	$1.54 \cdot 10^{-5}$

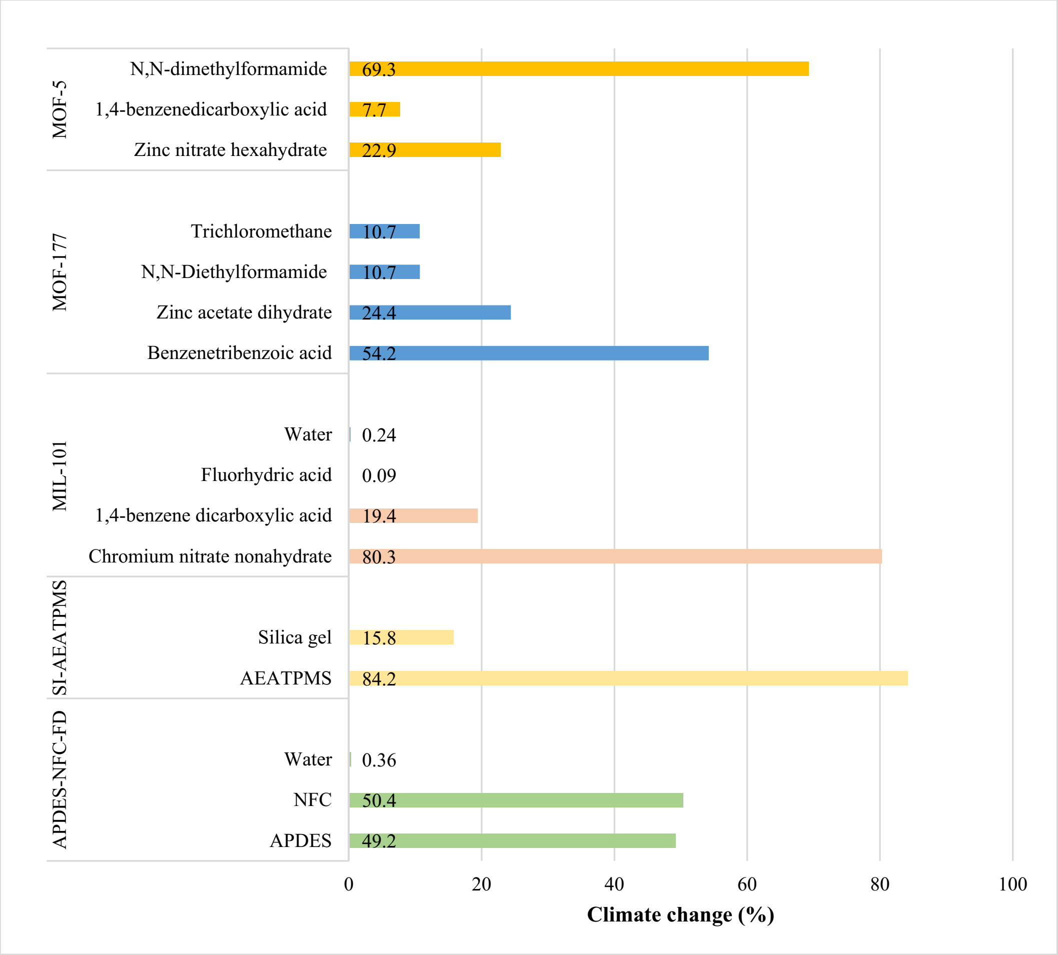

Fig. 2. Contribution to the overall climate change for: APDES-NFC-FD, SI-AEATPMS, MIL-101, MOF-177, MOF-5 production (1 kg) (SI=silica gel, AEATPMS = [N-(2-aminoethyl)-3 aminopropyl]trimethoxysilane, APDES = 3-aminopropylmethyldiethoxysilane, NFC = nanofibrillated cellulose).

In particular, these results from Table 9 suggest that to improve the SI-AEATPMS based process, it is essential to improve the physical properties of the sorbent, by increasing its carrying capacity (in terms of kg of CO_2 captured per kg of sorbent) in order to require a lower amount of sorbent mass that causes a lower burden on the environment. This could ensure a DAC system with a global warming potential (GWP) lower than that of the system based on APDES-NFC-FD, considering the best environmental performances of the SI-AEATPMS production, as reported in Section 3.1.

Table 9 shows that the thermal energy production from a municipal waste incinerator is a hotspot for the adsorption process while using the MIL-101 sorbent. The thermal energy production, with a value of 2.90×10^5 $kgCO_{2eq}$/tonne CO_2 captured, contributes most to the total CO_2 emissions of 4.33×10^5 $kgCO_{2eq}$/tonne CO_2, while the production of the sorbent is less significant. The modification of the MIL-101 sorbent by increasing the loading and working capacity as discussed in Section 3.1, could help to reduce the amount of heat for regeneration, hence reducing the impact of the MWI process on the total footprint.

Table 8
LCIA results for DAC adsorption processes capturing 1 tonne of CO_2 (SI=silica gel, AEATPMS = [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane, APDES = 3-aminopropylmethyldiethoxysilane, NFC = nanofibrillated cellulose).

Sorbent	MIL-101	MOF-177	MOF-5	APDES-NFC-FD	SI-AEATPMS
Climate change ($kgCO_{2eq}$)	$4.33 \cdot 10^5$	$5.30 \cdot 10^5$	$2.01 \cdot 10^5$	$-1.16 \cdot 10^2$	$6.25 \cdot 10^2$
Ozone depletion ($kgCFC11_{eq}$)	$2.98 \cdot 10^{-3}$	$1.10 \cdot 10^{-1}$	$1.61 \cdot 10^{-3}$	$5.86 \cdot 10^{-5}$	$2.69 \cdot 10^{-4}$
Ionizing radiation ($kBqU\text{-}235_{eq}$)	$5.93 \cdot 10^3$	$8.46 \cdot 10^3$	$3.12 \cdot 10^3$	$5.55 \cdot 10^1$	$2.08 \cdot 10^2$
Photochemical ozone formation ($kgNMVOC_{eq}$)	$4.95 \cdot 10^2$	$6.15 \cdot 10^2$	$2.32 \cdot 10^2$	1.14	2.48
Respiratory inorganics (disease incidences)	$2.87 \cdot 10^{-3}$	$3.70 \cdot 10^{-3}$	$1.36 \cdot 10^{-3}$	$1.05 \cdot 10^{-5}$	$3.06 \cdot 10^{-5}$
Non cancer human health effect (CTUh)	$1.48 \cdot 10^{-2}$	$1.77 \cdot 10^{-2}$	$7.26 \cdot 10^{-3}$	$3.59 \cdot 10^{-5}$	$1.69 \cdot 10^{-4}$
Cancer human health effect (CTUh)	$2.1 \cdot 10^{-2}$	$2.23 \cdot 10^{-2}$	$8.48 \cdot 10^{-3}$	$2.72 \cdot 10^{-5}$	$3.99 \cdot 10^{-5}$
Acidification terrestrial and freshwater ($molH^+_{eq}$)	$3.94 \cdot 10^2$	$5.13 \cdot 10^2$	$1.88 \cdot 10^2$	1.31	4.84
Euthrophication freshwater (kgP_{eq})	$3.82 \cdot 10$	$4.78 \cdot 10$	$1.82 \cdot 10$	$1.05 \cdot 10^{-2}$	$3.48 \cdot 10^{-1}$
Euthrophication marine (kgN_{eq})	$1.95 \cdot 10^2$	$2.43 \cdot 10^2$	$2.12 \cdot 10^2$	$4 \cdot 10^{-1}$	1.57
Euthrophication terrestrial ($molN_{eq}$)	$1.91 \cdot 10^3$	$2.45 \cdot 10^3$	$8.98 \cdot 10^2$	3.97	9.5
Ecotoxicity freshwater (CTUe)	$1.03 \cdot 10^6$	$1.22 \cdot 10^6$	$4.64 \cdot 10^5$	$1.42 \cdot 10^3$	$2.06 \cdot 10^3$
Land use (Pt)	$1.36 \cdot 10^5$	$3.39 \cdot 10^5$	$6.36 \cdot 10^4$	$4.76 \cdot 10^2$	$1.11 \cdot 10^4$
Water scarcity (m^3 depriv)	$3.08 \cdot 10^6$	$4.37 \cdot 10^6$	$1.6 \cdot 10^6$	$1.62 \cdot 10^4$	$9.44 \cdot 10^4$
Resource use, energy carriers (MJ)	$3.49 \cdot 10^5$	$5.12 \cdot 10^5$	$1.951 \cdot 10^5$	$3.81 \cdot 10^3$	$1.13 \cdot 10^4$
Resource use, mineral and metal ($kgSb_{eq}$)	$6.55 \cdot 10^{-2}$	$6.46 \cdot 10^{-2}$	$2.54 \cdot 10^{-2}$	$9.86 \cdot 10^{-4}$	$2.08 \cdot 10^{-3}$

Table 9

Contribution to the overall climate change for DAC adsorption processes using: APDES-NFC-FD, SI-AEATPMS, MIL-101, MOF-177, MOF-5 and capturing 1 tonne of CO_2 (SI=silica gel, AEATPMS = [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane,APDES = 3-aminopropylmethyldiethoxysilane, NFC = nanofibrillated cellulose, DAC=Direct Air Capture, MWI = Municipal Waste Incinerator).

	MIL-101	MOF-177	MOF-5	APDES-NFC-FD	SI-AEATPMS
Thermal energy from MWI ($kgCO_{2eq}$/tonne CO_2 captured)	$2.90 \cdot 10^5$	$3.52 \cdot 10^5$	$1.34 \cdot 10^5$	$3.88 \cdot 10^2$	$5.12 \cdot 10^2$
Electrical energy from MWI ($kgCO_{2eq}$/tonne CO_2 captured)	$1.42 \cdot 10^5$	$1.72 \cdot 10^5$	$6.56 \cdot 10^4$	$1.89 \cdot 10^2$	$2.50 \cdot 10^2$
Cooling water ($kgCO_{2eq}$/tonne CO_2 captured)	0	0	0	0	0
Sorbent production/disposal ($kgCO_{2eq}$/tonne CO_2 captured)	$1.02 \cdot 10^3$	$5.97 \cdot 10^3$	$1.79 \cdot 10^3$	$1.81 \cdot 10^2$	$6.99 \cdot 10^2$
DAC plant ($kgCO_{2eq}$/tonne CO_2 captured)	$-1.06 \cdot 10^2$	$-3.38 \cdot 10^2$	$-1.27 \cdot 10^2$	$-8.75 \cdot 10^2$	$-8.35 \cdot 10^2$
Overall climate change ($kgCO_{2eq}$/tonne CO_2 captured)	$4.33 \cdot 10^5$	$5.30 \cdot 10^5$	$2.01 \cdot 10^5$	$-1.16 \cdot 10^2$	$6.25 \cdot 10^2$

As for the SI-AEATPMS sorbent, reducing the required amount of sorbent could help to have lower carbon emissions, as well (reducing only the sorbent mass by 30%, results show that the climate change value is 416 $kgCO_{2eq}$/tonne CO_2 captured, about 33% lower than the base case).

The production/disposal of the other two MOFs (MOF-5 and MOF-177) is characterized by a higher value of GWP, causing a significant contribution to the overall carbon emissions of the overall process. However, the highest contribution is provided by the thermal energy production by MWI, with 3.52×10^5 $kgCO_{2eq}$/tonne CO_2 captured in the process using MOF-177 and 1.34×10^5 $kgCO_{2eq}$/tonne CO_2 captured in the system using MOF-5.

These results for these MOFs suggest reducing the amount of used sorbent and increasing its loading in order to decrease the burden on the environment.

In order to verify that net negative emissions are present for a closed system (implying a removal of CO_2 from the atmosphere), we supposed that the captured CO_2 is stored (cradle-to-grave analysis). The electrical energy consumption for CO_2 storage is 0.101 kWh/$kgCO_2$ (Deutz and Bardow, 2021), while the grid electricity emission factor for Switzerland is 0.171 $kgCO_{2eq}$/kWh (Thinkstep, 2020). Then, to store 1 tonne of CO_2, 17.3 $kgCO_{2eq}$ are emitted: for the cradle-to-grave process using the APDES-NFC-FD sorbent, the overall value of climate change is −98.7 $kgCO_{2eq}$/tonne CO_2 captured and stored. The negative value suggests that the removal of CO_2 from the atmosphere is ensured by this technology and particular sorbent.

The values of climate change according to a cradle-to-grave analysis for the other systems using MOFs are significantly unchanged while for the system using the SI-AEATPMS sorbent the climate change value is 642 $kgCO_{2eq}$/tonne CO_2 captured and stored.

It is interesting to compare the results of the cradle-to-gate analysis with those related to the absorption technology (e.g. Carbon Engineering technology) reported by Skone (2021) and for which −390 $kgCO_{2eq}$/tonne CO_2 captured are obtained from the environmental analysis (cradle-to-gate) by using the potassium hydroxide solution. According to the results reported here, the absorption technology ensures a lower environmental impact compared to the DAC process using an APDES-NFC-FD sorbent and showing −116 $kgCO_{2eq}$/tonne CO_2 captured and then compared to other systems using the other investigated sorbents. Thus, a better environmental performance is for the absorption technology, despite the increased complexity. However, both technologies should be compared on an exact like-for-like modeling basis to be certain of the relative environmental performance.

Considering other impact categories, results show that the capturing system using the cellulose based amine sorbent has also the lowest environmental impact. A difference with the other systems is reported in Table SI 21 of the Supporting information. On the other hand, the DAC systems using MOFs as sorbents should not be used, due to a large required energy consumption that produces a high environmental impact. The use of these sorbents is therefore not recommended for the analyzed process, and may never be valuable.

The process using APDES-NFC-FD has the least impact on resource use, energy carriers ($3.81 \cdot 10^3$ MJ/tonne CO_2 captured) compared to MOF-177 ($5.12 \cdot 10^5$ MJ/tonne CO_2 captured). Similarly, the use of APDES-NFC-FD ensures a lower land use impact ($4.76 \cdot 10^2$ Pt/tonne CO_2 captured) compared to the MOF-177 use ($3.39 \cdot 10^5$ Pt/tonne CO_2 captured). For the first process, the values of ozone depletion, ionizing radiation and photochemical ozone formation are respectively of $5.86 \cdot 10^{-5}$ $kgCFC11_{eq}$/tonne CO_2 captured, $5.55 \cdot 10^1$ kBqU-235_{eq}/tonne CO_2 captured and 1.14 $kgNMVOC_{eq}$/tonne CO_2 captured. For these impact categories, the highest values are respectively obtained for the system using MIL-101 ($2.98 \cdot 10^{-3}$ $kgCFC11_{eq}$/tonne CO_2 captured), MOF-177 ($8.46 \cdot 10^3$ kBqU-235_{eq}/tonne CO_2 captured) and MOF-177 (615 $kgNMVOC_{eq}$/tonne CO_2 captured). Highest values of respiratory inorganics ($3.7 \cdot 10^{-3}$ disease incidences/tonne CO_2 captured), non cancer human health effect ($1.77 \cdot 10^{-2}$ CTUh/tonne CO_2 captured), cancer human health effect ($2.23 \cdot 10^{-2}$ CTUh/tonne CO_2 captured), acidification terrestrial and freshwater ($5.13 \cdot 10^2$ $molH^+_{eq}$/tonne CO_2 captured) and euthrophication freshwater (47.8 kgP_{eq}/tonne CO_2 captured) are reported by the DAC plant using MOF-177.

The highest value for euthrophication marine is obtained for the system based on MOF-177 ($2.45 \cdot 10^3$ kgN_{eq}/tonne CO_2 captured). The DAC process based on MOF-117 has also the greatest value for euthrophication terrestrial ($2.45 \cdot 10^3$ $molN_{eq}$/tonne CO_2 captured) and ecotoxicity freshwater ($1.22 \cdot 10^6$ CTUe/tonne CO_2 captured). Water scarcity has the greatest value in the process using MOF-177 ($4.37 \cdot 10^6$ m^3 depriv/tonne CO_2 captured) while the greatest value for resource use, mineral and metal is for the system using MIL-101 ($6.55 \cdot 10^{-2}$ $kgSb_{eq}$/tonne CO_2 captured).

3.3. Sensitivity analysis

Regarding the last step of this LCA, a sensitivity analysis was conducted for the described system in Section 2.1. Initially here, we considered a future energy system characterizing the heat and electricity sources supplied to the DAC system according to the future forecast (2050), as presented in Table SI 22 of the Supporting information, keeping constant the inventory data of DAC. Data in Table SI 22 show that by 2050 heat may be produced mostly by electricity to power these systems, while electrical energy will be produced mostly from renewable sources.

Results, reported in Table SI 23 of the Supporting information, show that the use of a future energy system could reduce the value of climate change impact for all analyzed systems, although only the DAC process using the cellulose based amine sorbent allows negative CO_2 emissions. However, considering other impact categories (mostly ozone depletion, ionizing radiation, photochemical ozone formation, respiratory inorganics, non cancer human health effect, land use, water scarcity, resource use) a higher environmental impact is caused by the future energy system, demonstrating the benefits of the use of “waste heat” from a MWI. Additional research should be conducted to consider the supply of energy in 2050, in order to lower the environmental burden, and not only in term of CO_2 emissions.

Another sensitivity analysis was carried out by changing the sorbent mass. This was because the DAC process based on APDES-NFC-FD was still the only plant with negative carbon emissions as demonstrated by

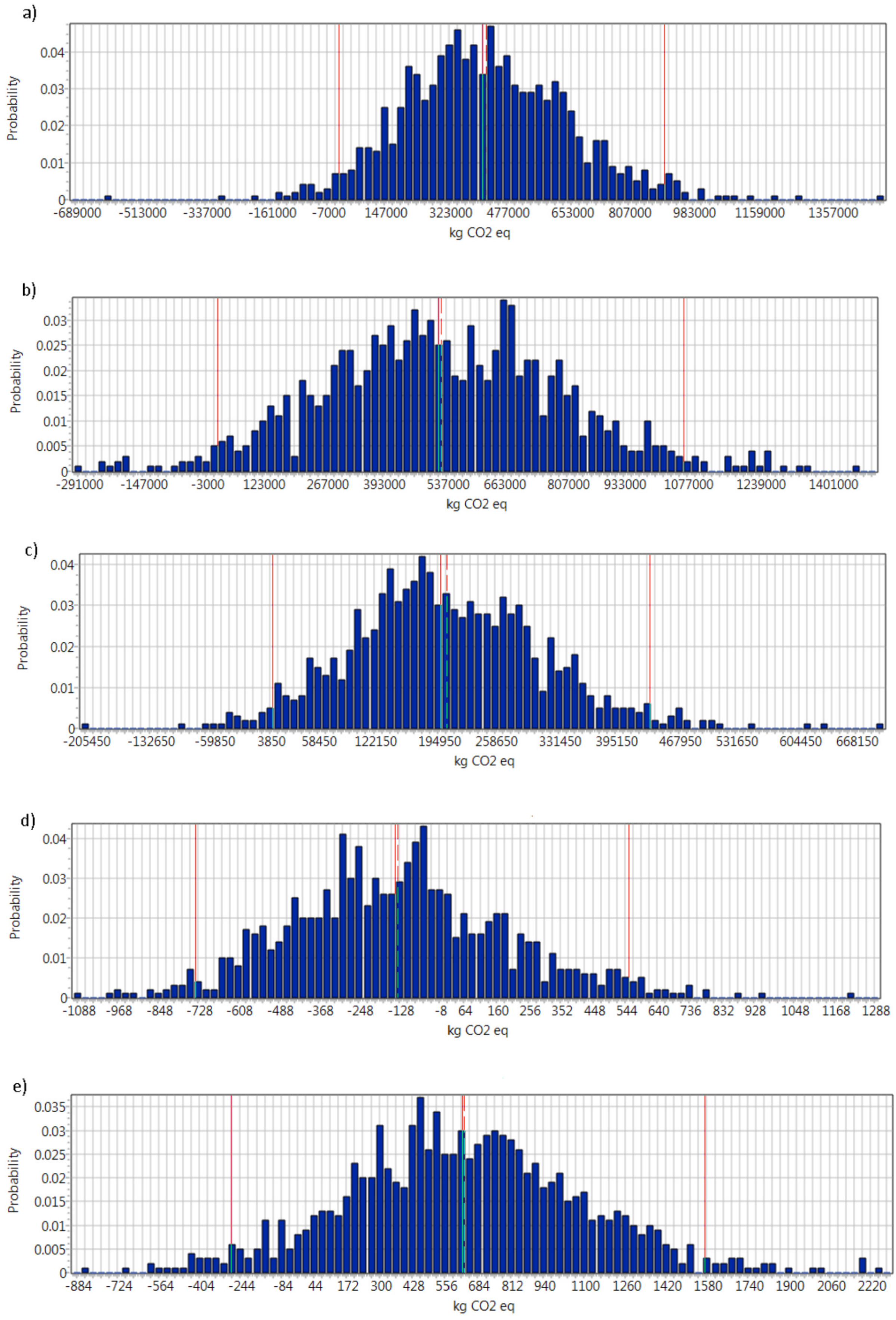

Fig. 3. Monte Carlo simulation results for climate change for DAC adsorption processes using: a) MIL-101, b) MOF-177, c) MOF-5, d) APDES-NFC-FD, e) SI-AEATPMS.

results from previous above case study. A Monte Carlo simulation was also conducted using SimaPro software by varying the sorbent mass (±/-30% of base case value) and in addition to this the heat requirement (±/-50% of base case value) and electricity requirement (±/-30% of base case value) because these have an important contribution to the overall climate change especially for systems using MOFs. The range was selected according to the variation of heat and electricity supply needed today and in the future, reported by Deutz and Bardow (2021). The variation of sorbent mass it was assumed to be the same of that of the electricity, as the two parameters are correlated. A normal distribution was assumed for these inputs. An uncertainty range scenario in input factors propagates to a distribution in the output value as in Fig. 3, while the 95% of results are in the range reported in Fig. 4.

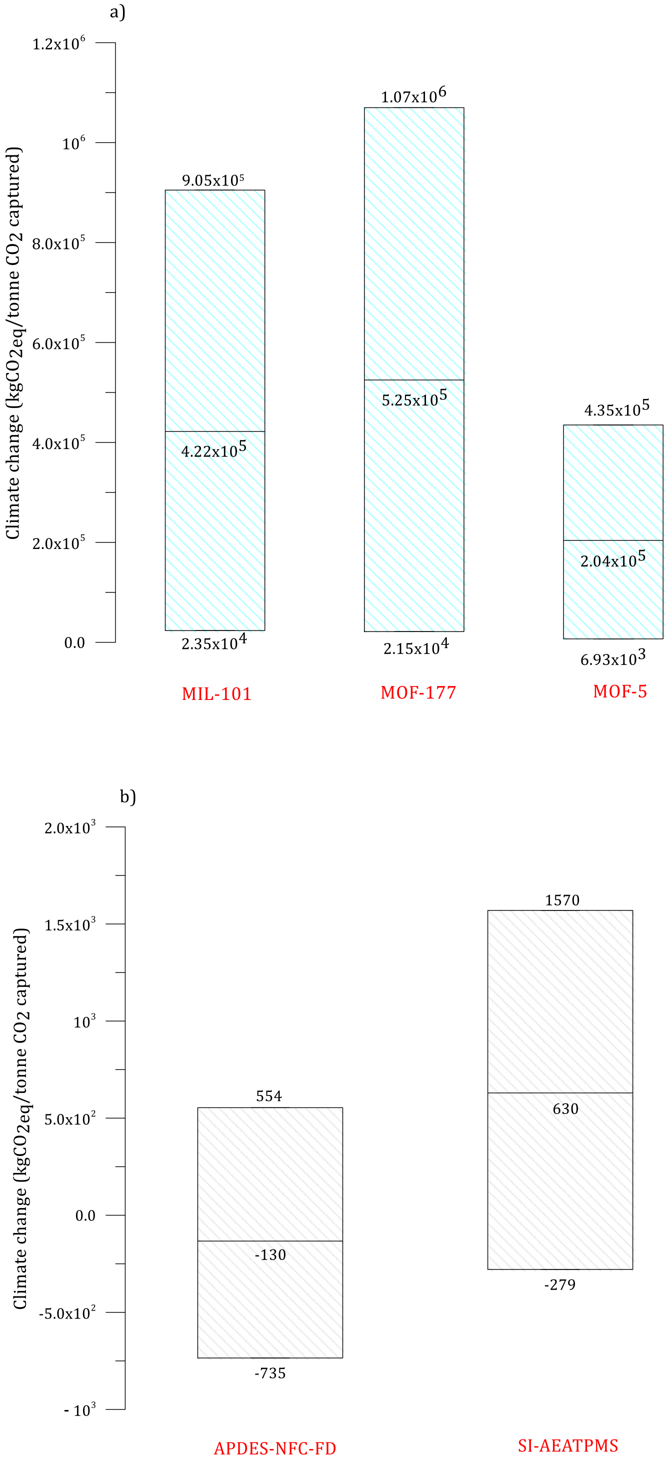

Fig. 4. Results of Monte Carlo simulation: 95% confidence interval for the climate change impact category for a) MOFs based systems; b) amine functionalized sorbents based systems (SI=silica gel, AEATPMS = [N-(2-aminoethyl)-3-aminopropyl]trimethoxysilane, APDES = 3-aminopropylmethyldiethoxysilane, NFC = nanofibrillated cellulose).

It is evident that at the lowest level of investigated parameters, the two DAC systems with amine functionalized sorbents have a defined probability to have negative CO_2 emissions. Then as suggested in Section 3.2 increasing the uptake of the silica gel-based amine sorbent could decrease the carbon footprint impact to a negative value. A more significant variation of the investigated parameters is required for MOF-based processes to allow negative CO_2 emissions. The very large required improvements may mitigate away from such processes for CO_2 capture from the air.

4. Conclusions

In this study, an independent LCA of DAC adsorption processes was designed and conducted based on previous research (Leonzio et al., 2022) which studied a plant capturing CO_2 from the air, constructed and operated by Climeworks. This work was necessitated by the lack of transparency and utilization of proxy data in the few existing literature studies. Two amine functionalized sorbents (SI-AEATPMS and APDES-NFC-FD) and three MOFs (MIL-101, MOF-177 and MOF-5) were considered as the adsorbent beds. The aim of this analysis was to verify that a DAC adsorption process, using these sorbents, could effectively remove CO_2 from the atmosphere, while helping to achieve targets fixed for the future.

Our results show that the production of SI-AEATPMS has the lowest carbon footprint, whereas SI-AEATPMS and MIL-101 have the lowest environmental impacts, considering other impact categories. Synthesis routes of MOFs, that are based not on organic solvents, are required to lower their burden.

Regarding the DAC adsorption plants, according to a cradle-to-gate analysis, we found that the process using APDES-NFC-FD, as in the Climeworks plant, has a negative value of climate change impact and the best performance considering other impact categories. Moreover, considering a cradle-to-grave system with the storage of CO_2, the removal of CO_2 from the atmosphere is ensured by this particular system and sorbent and a more efficiency will be ensured by using more adsorbent beds. The DAC plants using physisorbents have worse results, due to a higher amount of sorbent and associated energy consumptions. Chemisorbents ensure not only better operating conditions, but also a lower environmental impact compared to physisorbents.

Future research should be focused on improving the physical properties and performances of the silica gel-based amine sorbent with the aim to reduce the required mass, considering that its production has relatively low environmental cost. By increasing the carrying capacity for CO_2 of this sorbent, in terms of kg of CO_2 per kg of sorbent, the capture process can have a lower environmental burden, which could be competitive with that of a process using APDES-NFC-FD. Research on MOFs will need to reduce sorbent mass requirements, as for SI-AEATPMS, and increase the loading to reduce energy consumptions.

The use of a future energy system, such as that predicted to be in place by 2050 for DAC plants shows that CO_2 emissions are reduced, but other impact categories have worse results. Further studies are still required to examine further sources of improvement when future energy sources are used.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.spc.2022.04.004.

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