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CO_2 in indoor environments: from environmental and health risk to potential renewable carbon source

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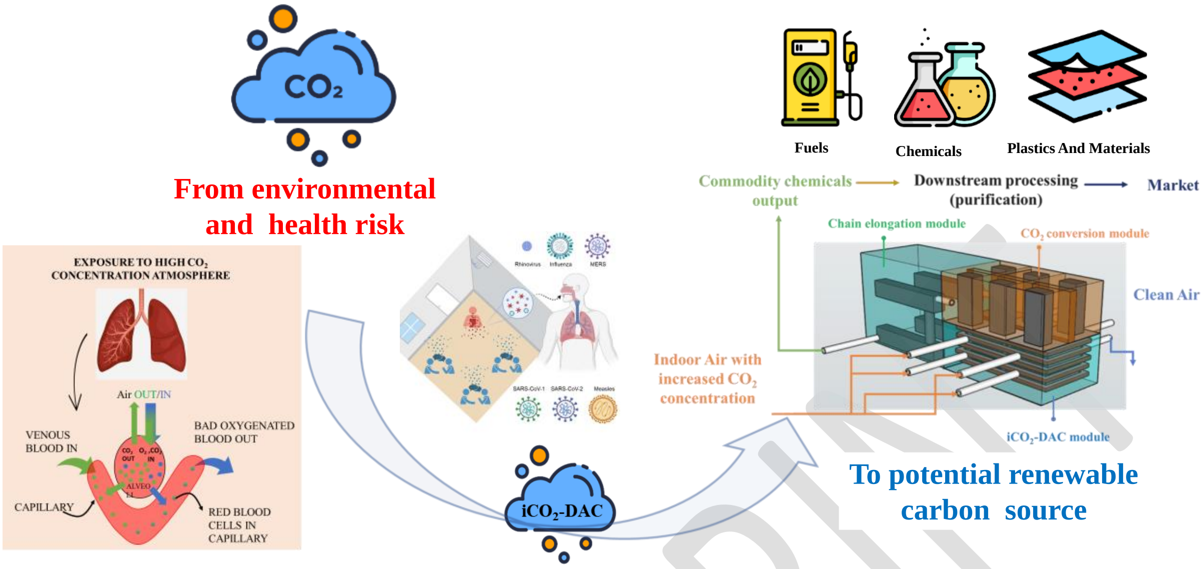
Highlights

- Environmental pressure requires further use of renewable energy and carbon sources
- Indoor CO_2 from Direct Air Capture is assessed as potential renewable carbon feedstock
- Environmental and health risks associated to CO_2 exposure are presented
- Factors influencing CO_2 concentration in representative indoor air are reviewed
- Envisioned solutions aim to capture indoor air pollutants to transform them into green chemicals

Graphical abstract



Abstract

In the developed world, individuals spend most of their time indoors. Poor Indoor Air Quality (IAQ) has a wide range of effects on human health. The burden of disease associated with indoor air accounts for millions of premature deaths related to exposure to Indoor Air Pollutants (IAPs). Among them, CO_2 is the most common one, and is commonly used as a metric of IAQ. Indoor CO_2 concentrations can be significantly higher than outdoors due to human metabolism and activities. Even in presence of ventilation, controlling the CO_2 concentration below the Indoor Air Guideline Values (IAGVs) is a challenge, and many indoor environments including schools, offices and transportation exceed the recommended value of 1000 ppm_v. This is often accompanied by high concentration of other pollutants, including bio-effluents such as viruses, and the importance of mitigating the transmission of airborne diseases has been highlighted by the COVID-19 pandemic. On the other hand, the relatively high CO_2 concentration of indoor environments presents a thermodynamic advantage for direct air capture (DAC) in comparison to atmospheric CO_2 concentration. This review aims to describe the issues associated with poor IAQ, and to demonstrate the potential of indoor CO_2 DAC to purify indoor air whilst generating a renewable carbon stream that can replace conventional carbon sources as a building block for chemical production, contributing to the circular economy.

Keywords: climate change, Indoor air quality, health risk, CO_2 capture, renewable energy, biofuels, microbial electrochemical technologies

Contents

1. Motivation: The Need For Renewable Carbon Sources

1.1. Climate Change Emergency: A Serious Challenge With Present And Future Consequences

Climate change is increasing the frequency and the intensity of extreme weather events such as heatwaves, droughts, floods and tropical cyclones, aggravating water management problems, damaging critical infrastructures, and interrupting the provision of basic services such as water and sanitation, education, energy, and transport (Keim, 2019). Some effects of climate change can already be quantified and are summarized in Table 1.

Table 1
Summary of climate change effects

Effect	**Period**	**Reference**
The average global temperature increased by 0.85 ºC	1880-2012	Intergovernmental Panel on Climate Change, 2021
Oceans level rose by 19 cm as oceans expanded	1901-2010	Church et al., 2013
Arctic's Sea ice extent has shrunk at a 13.1% per decade	1979-2020	Landrum and Holland, 2020
CO_2 concentration in the atmosphere has increased from the pre-industrial 277 ppm_v to 407.8 ppm_v	1750-2018	Le Quéré et al., 2019
Greenhouse gas emissions (GHG) grew at an average of 1 Gt CO_2eq (2.2%) per year between 2000 and 2010, compared to 0.4 Gt CO_2eq (1.3%) per year between 1970 and 2000	1970-2000 2000-2010	Intergovernmental Panel on Climate Change, 2015

The latest Intergovernmental Panel on Climate Change (IPCC) report states that unless there are immediate, rapid, and large-scale reductions in GHG emissions, limiting global warming to close to 1.5 ºC or even 2 ºC will be beyond reach (Intergovernmental Panel on Climate Change, 2021). GHGs such as methane and nitrous oxide have a 25 and 298-fold higher global warming potential (GWP) than CO_2, respectively (Forster et al., 2007; Huang et al., 2013). However, CO_2 is the most common GHG emitted by human activities, in terms of quantity released and the total impact on global warming. In the US in 2019, CO_2 accounted for about 80% of GHG emissions (US EPA, 2021a), which was 15% of the global emission, behind China with 30% (Olivier and Peters, 2020).

Over the past decades, the European Union (EU) has taken essential steps toward achieving its goal of climate neutrality by 2050. Since 1990, GHG emissions in the EU have been steadily declining. In 2018, GHG emissions in the EU-28 have fallen 23% below 1990 levels (European Environment Agency, 2019). Actions taken by the EU, including a rapid decarbonization of the power sector, deployment of renewable energy and improvements in energy efficiency, together with an increasing public awareness of climate change effects, helped the EU to reach the 2020 targets (Directorate-General for Research and Innovation, 2018; Eureopean Commission, 2021a). In 2020, GHG emissions dropped further due to the COVID-19 forced confinement, resulting in the largest-ever decline in global GHG emissions (Andreoni, 2021; Han et al., 2021). Daily CO_2 emissions decreased by 17% by early April 2020 compared with the mean of 2019 levels, with a 26% decrease on average during the pandemic peak (Le Quéré et al., 2020). However, this improvement was only temporary and global GHG emissions continue a relentless rise. Forecasts anticipate that fossil fuel consumption and CO_2 emissions will return to the pre-pandemic levels, and even exceed them (Smith et al., 2021). Such rebound effect in global carbon emissions after COVID-19 crisis is a stark warning that not enough is being done to accelerate the clean energy transition worldwide.

1.2. Climate Change Mitigation through Circular Economy Strategies

To efficiently and permanently fight climate change, short-term (NewClimate Institute et al., 2016) and middle-term (UNEP, 2018) actions must be aligned with long-term goals to achieve durable transformation (Falduto and Rocha, 2020). The development of new policies against GHG emissions, *i.e.* the cap and trade policy adopted in the EU since 2005 (European Commission, 2020) and incentives towards green infrastructure (Forster et al., 2020), are strongly needed.

One path towards sustainability is the adoption of a circular economy over the inefficient linear “take-make-waste” economic model. Circular economy is defined as a regenerative system in which resource input and waste, emission, and energy leakage are minimized by slowing, closing, and narrowing material and energy loops. This can be achieved through long-lasting design, maintenance, repair, reuse, remanufacturing, refurbishing, and recycling (Geissdoerfer et al., 2017). The Circularity GAP Report highlights the vast scope to reduce GHG emissions by applying circular principles- notably re-use, re-manufacturing and recycling. A circular economy intends to maximize the use of existing assets, while reducing dependence on new raw materials and minimizing waste (Christis et al., 2019).

According to the Circular Economy Action plan guidelines developed by the European Commission, the transition from linear to circular economy must be driven by research, innovation and digitalization (European Commission, 2020a). The European Regional Development Fund, through its smart specialization, LIFE and Horizon Europe research programmes aim to complement private funding and support the whole innovation cycle. One of the aims of the Horizon Europe program within the Circular Economy Action plan is the development of novel materials and products, new production and recycling technologies, including exploring the potential of chemical recycling.

1.3. Renewable Carbon-Sources: From Waste to a Sustainable Solution

Through the Paris Agreement of December 2015, signing governments have implicitly agreed to dramatically reduce the use of fossil fuels over the coming decades (Piggot et al., 2020). Later, in July 2021, the EU adopted legislative proposals to achieve climate neutrality by 2050, with an intermediate target of 55% net reduction in GHG emissions by 2030 (European Commission, 2021b). Climate neutrality is defined as the reduction of GHG emissions in all sectors to reach an absolute net-zero emission level (Arikan et al., 2020). This implies moving away from fossil fuels such as crude oil and coal, which are still the main energy sources (79%) (IEA, 2020; Singh et al., 2020) and the prevalent feedstock consumed in the chemical industry (85%) (Levi and Cullen, 2018; Skoczinski et al., 2021), towards clean energy sources such as wind, water and solar power, among others (Directorate-General for Research and Innovation, 2018; European Comission, 2020b; European Environment Agency, 2019; Leonard et al., 2020).

Unlike the energy sector, the chemical and materials industry is essentially carbon-based and has no alternative to carbon sources as feedstock (Lee, 2019). This irreplaceability of carbon is due to the production of materials largely linked to the presence of carbon in their chemical composition (Cazorla-amorós, 2014; Nesbitt, 2020). Thus, it is of high importance to find greener and sustainable carbon sources for a transition to renewable carbon in the next years (Ángel et al., 2021).

Carus et al. (2020a) defined as renewable carbon all the carbon sources that avoid or substitute fossil carbon from the geosphere. According to the Renewable Carbon initiative, there are only three sources of renewable carbon (Figure 1). The first one comes from the biosphere, and can be re-grown, such as all types of biomasses (food crops, non-food crops, side streams, by-products and biogenic waste) (Kalt et al., 2021; Serrano-ruiz, 2020). Using biomass as feedstock is potentially carbon neutral since plants harvest CO_2 during their growth, which is released back upon combustion of biomass-based products such as biofuels (Popp et al., 2014; Sheldon, 2011).

The second source of renewable carbon comes from the techno-sphere, and is obtained by recycling carbon-containing products such as plastics at the end of their life cycle (Bachmann et al., 2021; Shamsuyeva and Endres, 2021). Recycling is performed by chemical technologies that break down polymeric materials to monomers or larger polymerizable units, or fragments from which polymers or other useful products can be made (Chanda, 2021; Rickert et al., 2020). Recycling carbon-containing products can help bringing businesses closer to shaping a circular economy (Meys et al., 2020). Waste that can be recycled and injected back into the economy as secondary raw material to substitute and reduce virgin materials consumption, allowing to deliver the same, or a better, output with less material input (European Comission, 2020a; Haigh et al., 2021). .

The third source of renewable carbon is the CO_2 that comes either from the techno-sphere or the atmosphere, which can be captured from the exhaust gas of industries (Gabrielli et al., 2020; Kätelhön et al., 2019; Naims, 2016), or directly from the atmosphere, providing an almost endlessly available resource (Goeppert et al., 2012a; Marchese et al., 2021; Schellevis et al., 2021). The carbon cycle can be closed by converting industrially emitted or atmospheric CO_2 using carbon capture and utilization (CCU) technologies.

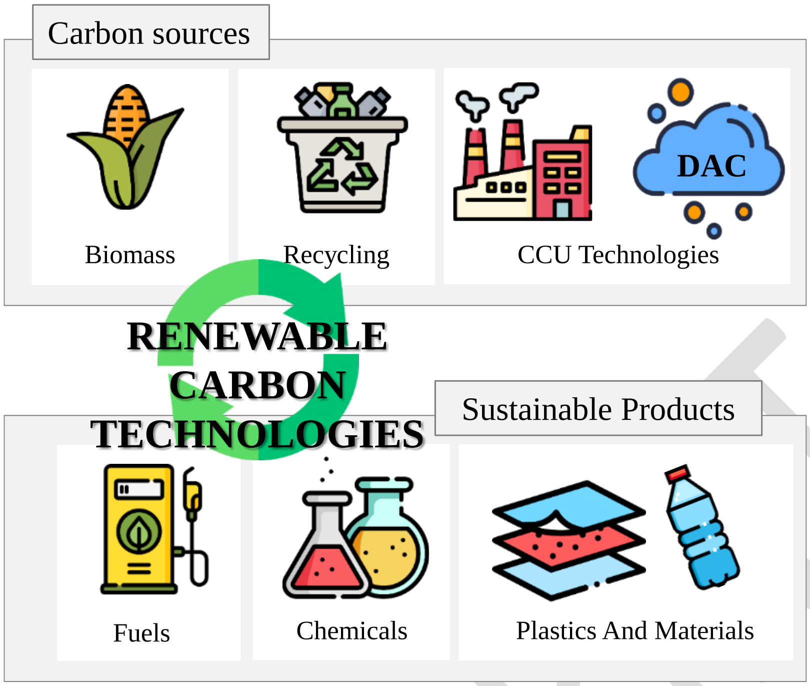


Fig. 1. Schematic overview of the renewable carbons sources At the top: i) biomass (food crops, non-food crops, side streams, by-products and biogenic waste), ii) recycling of carbon-containing products such as plastics, and iii) CO_2 capture from flue gases and direct air capture (DAC); at the bottom, the sustainable products that can be obtained from renewable carbon sources. Figure adapted from Renewable energy and renewable carbon (Carus et al., 2020a).

1.4. Carbon Capture And Utilization Technologies: Turning Waste Into Building Blocks For A Sustainable Future

Carbon Capture and Storage (CCS) and CCU technologies are increasingly important for mitigating CO_2 emissions difficult to avoid (Bruhn et al., 2016; Wang et al., 2020), and minimizing the extraction of carbon from the geosphere (Carus et al., 2020a). CCS uses a combination of technologies to capture the CO_2 released from fossil fuel usage and transport it to safe and permanent storage locations (Wilberforce et al., 2021; Zhang et al., 2014). Such technology is aimed at CO_2 emissions from large point sources such as power plants, cement plants, oil refineries, and iron or steel industry installations (Sanz-Pérez et al., 2016; Valentić et al., 2016; Yang et al., 2021; Zhu, 2019). Dessì et al. (2021) summarized CO_2 emissions for specific industries such as steel mills (20-30 vol. % CO_2), ceramic (20-30 vol. % CO_2), glass (10-15 vol. % CO_2), refineries (10-20 vol. % CO_2), cement industries (15-20 vol. % CO_2) and power plants (10-15 vol. %

CO_2). Other gases such as biogenic gas from fermentation and oxy-fuel combustion outlet present CO_2 content higher than 90 vol. %.

Although CCS play an important role in mitigating CO_2 emissions from large sources, (Peridas and Schmidt, 2021; Tamme, 2021), the IPCC AR4 reported that even under an ideal scenario, CCS technologies would at the most slow down the increase of CO_2 concentration in the atmosphere (Metz et al., 2005; Solomon et al., 2007). CCS technologies advantages and challenges are summarized in Table 2.

The challenges that CCS technologies have to overcome result in a lack of financial support that delays their implementation worldwide (Lupion et al., 2015; Shirmohammadi et al., 2020). Moreover, there is a significant social scepticism partly due to poor communication efforts in demonstration projects (Bui et al., 2018; De Coninck and Benson, 2014). Consequently, there has been a shift from CCS paradigm to CCU, particularly in Europe (Sayari et al., 2016). However, CCU technologies are much more complicated than CCS technologies, primarily due to the inert nature and high thermodynamic stability of CO_2 (Sakakura et al., 2007), the high energy input required, and the control of complex processes (Cuéllar-Franca and Azapagic, 2015). The main advantage of CCU over CCS is that utilization of CO_2 is a profitable activity that produces a variety of products (Styring et al., 2011).

Table 2.
CCS technologies advantages and challenges

	Description	**Reference**
Advantage	Mitigate CO_2 emissions difficult to avoid	Wang et al., 2020
	Avoid the extraction of carbon from the geosphere	Carus et al., 2020
	No risk of fires that can release CO_2 stored in biomass into the atmosphere	Tamme, 2021
	Can be integrated into existing energy systems without requiring large amendments	Bui et al., 2018
	Can be combined with low-carbon or carbon-neutral bioenergy to generate negative emissions	Fuss et al., 2014
Challenge	Large parasitic load because of the low concentration of CO_2 in combustion flue gases, between 10-15% from coal power and 4-5% for natural gas-fired power plants	Global CCS Institute, 2012; Salvi and Jindal, 2019
	High cost of concentrating CO_2 (above 95.5% needed for transport and storage)	Brownsort, 2019; Wetenhall et al., 2014
	Uncertainties in quantifying leakages rates and expected economic and environmental cost of leakage	Deng et al., 2017; Vinca et al., 2018

CCU technologies aim to capture CO_2, either from industrial point sources or directly from the air, and transform it into valuable chemical building blocks, synthetic fuels or construction materials (CO_2 Value

Europe, 2021). CCU technologies can convert CO_2 into fine chemicals with high market value such as methylurethane, 2-oxazolidone and isopropyl isocyanate (Yang et al., 2021) or bulk chemicals such as formic acid (Leitner, 1995), methanol (Pontzen et al., 2011), acetic acid (Gildemyn et al., 2015), urea (Xiaoding and Moulijn, 1996), butyrate (Batlle-Vilanova et al., 2017) among others.

The scale of fixation for a specific product is an important factor regarding CCU technologies (Yu et al., 2008). While fine chemicals, or those of pharmaceutical interest, have limited demand from hundreds of tons annually, other production lines can have a higher impact on the overall worldwide carbon emissions. CO_2 can be used to produce chemicals that can store chemical energy like methanol, dimethyl carbonate (DMC) and dimethyl ether (DME) (Ganesh, 2011; Razali et al., 2012), while fuels such as light olefins and liquid hydrocarbons can be produced from direct hydrogenation of CO_2, similarly to the Fischer-Tropsch reaction of CO and H_2 (Sakakura et al., 2007; Steynberg, 2004). Another CCU technology that has shown a significant impact on carbon emissions is Mineral Carbonation Technology (MCT). In MCT, CO_2 is chemically reacted with calcium and/or magnesium-containing minerals to form carbonate materials (Olajire, 2013). MCT can be considered both CCS and CCU, however, the latter applies if the intended application of carbonate goes beyond storing CO_2, by using it as a material in the construction industry (Bodor et al., 2013; Ghiat and Al-Ansari, 2021; Woodall et al., 2019).

CCU pathways are mainly divided into five wide-ranging categories as summarized in Table 3 (Ghiat and Al-Ansari, 2021). Some authors consider enhanced oil recovery (EOR) and enhanced gas recovery (EGR) as a direct utilization of CO_2, where it is injected into depleted oil and natural gas fields (Norhasyima and Mahlia, 2018), while others argue their inclusion as CCU technologies because EOR and EGR may foster the continued use of fossil fuel resources in combination with carbon capture (Olfe-Kräutlein, 2020). Chauvy et al. (2019) proposed a simpler CCU classification with two big categories: direct use of CO_2, and CO_2 conversion. A large number of research studies on CCU technologies based on CO_2 conversion have been published recently (Dessì et al., 2021; Guzmán et al., 2021; McQueen et al., 2021; Rovira-Alsina et al., 2021; Schievano et al., 2019), principally motivated by the increase of political and public awareness about climate change.

Table 3.
CCU technologies classification

Category	Example	Product	Reference
Conversion to chemicals and fuels	CO_2 recycling platform based on two separated steps (bioelectrosynthesis and fermentation)	First step: acetic acid and ethanol; second step: butyric and caproic acid	Romans-Casas et al., 2021
Mineral carbonation	Mineral carbonation of pulp and paper industry waste	Calcium carbonates ($CaCO_3$)	Spínola et al., 2021
Enhanced oil recovery (EOR) and enhanced gas recovery (EGR)	Inject CO_2 into the oil and gas reservoirs to recover the oil trapped in the rocks.	Oil and Gas	Norhasyima and Mahlia, 2018
Biological conversion	CO_2 absorption and fixation by algae and other terrestrial crops via the photosynthesis process	Biofuel production, animal feed	Pahunang et al., 2021
Direct CO_2 utilization	CO_2 is used as a refrigerant, for carbonation of beverages, and food preservation	Food and beverage industry	Zhu, 2019

Although CCS technologies mostly aim at CO_2 emissions from large point sources (Zhang et al., 2014), CO_2 also originates from numerous other sources, including medium-scale CO_2 releasing sources from commercial and industrial buildings and small sources such as the transportation sector (Ghiat and Al-Ansari, 2021; Rossing and Chiaverina, 2019). Between one-third and one-half of total CO_2 emissions are associated with billions of distributed sources such as vehicles, airplanes, and furnaces used in residential and commercial buildings (Lackner et al., 2012). Hence, more attention is needed towards capturing CO_2 directly from the atmosphere.

1.5. CO_2 From Direct Air Capture As Renewable Carbon Feedstock

Direct Air Capture (DAC) is a promising approach for atmospheric Carbon Dioxide Removal (CDR) firstly introduced by Lackner et al. (1999), although several authors claim that technologies for air purification have been introduced already in the 1940s and 1950s for use in submarines and spacecrafts (Sanz-Pérez et al., 2016; Satyapal et al., 2001; Tepe and Dodge, 1943). Beuttler et al. (2019) defined DAC as a range of technological solutions to extract CO_2 from ambient air at any location on the planet In particular, the purpose of DAC technologies is to capture CO_2 from air and produce a more concentrated stream of CO_2

for storage or utilization (McQueen et al., 2021). Originally, the cost of DAC was argued to be prohibitively high (Herzog, 2003) as a result of the extreme dilute nature of atmospheric CO_2 (Bui et al., 2018). However, recent reports demonstrate that DAC has a sufficient technical maturity for economic feasibility (Keith et al., 2018). According to the International Energy Agency (IEA) there are 15 DAC plants operating worldwide, where the primary industrial developers are Carbon Engineering (Canada), Climeworks (Switzerland), and Global Thermostat (USA) (McQueen et al., 2021). Unlike CO_2 capture from flue-gas, DAC does not operate in the presence of high levels of contaminants (SO_x, NO_x, and mercury), as occurs in many industry emissions, and does not need to achieve near-complete CO_2 removal in a single pass.

Special focus in the field of DAC technologies has been placed towards sorbent selection (Azarabadi and Lackner, 2019; Goeppert et al., 2012a; Sanz-Pérez et al., 2016), unit operation design (Lackner, 2013; Wurzbacher et al., 2016; Zhang et al., 2014) or basic process development (Bretherton, F. and Bretherton, 1961; Goeppert et al., 2012a; Mazzotti et al., 2013). According to Schellevis et al., two major technologies are considered for DAC on commercial scale (Schellevis et al., 2021): absorption using alkaline solutions where aqueous KOH is the capture medium and a calcium caustic loop is used to recover CO_2 (Keith et al., 2018; Lackner et al., 1999), and adsoption using amine-functionalized solid sorbents, in which CO_2 reacts with amine-groups on the internal surface of the sorbent and then CO_2 is recovered by a temperature and/or vacuum swing (Bos et al., 2019; Elfving et al., 2021). The majority of DAC studies with sorbents have focused on solid-supported amine materials (Sanz-Pérez et al., 2016; Schellevis et al., 2021). Aqueous solvent-based approaches typically require high temperatures (over 800 ºC) and an oxygen atmopshere to recover CO_2 as calcium carbonate, and to regenerate the alkaline sorbent (Williams and Custelcean, 2020). Furhtermore, due to the low CO_2 concentration in air, the energy penalty caused by the latent and sensible heat required to desorb CO_2 from the alkaline medium is higher than the separation from solid sorbents (McQueen et al., 2021; Zhang et al., 2016). DAC using amine-specialized sorbents is thus less energy intensive, as the desoprtion process can be carried out at milder temperatures (below 110 ºC) (Goeppert et al., 2014, 2012a). The mild operating conditions of amine-specialized sorbents makes them suitable for capturing CO_2 from enclosed spaces such as submarines (Carey et al., 1983; Lackner et al., 1999) and spaceships (Carey et al., 1983; Satyapal et al., 2001), which opens the door to explore the application of CO_2 DAC into other types of indoor spaces. As suggested by Modak et al. (2020), DAC has a wide scope for implementation in enclosed environments, which has remained unexploited to date, although research on novel materials is still limited. This technology can only be implemented on a broad scale if CO_2 selective, abundant, sustainable and low-cost materials are developed. Further details about technical (Al-Absi et al., 2022; Goeppert et al., 2014, 2012b; Sanz-Pérez et al., 2016) and economic feasibility of CO_2-DAC can be found elsewhere (Chen and Tavoni, 2013; Daniel et al., 2022; Socolow et al., 2011; Wang et al., 2013; Zhang et al., 2014).

The main goal of this review is to assess the potential of CO_2 from indoor air environments as a renewable carbon source to minimize, reduce and ultimately substitute fossil fuel carbon sources. Specifically, this work provides insights on indoor air quality, focusing on the health effects of CO_2 and other indoor air pollutants in three representative indoor environments (school classrooms, office environments and underground transport vehicles), examining them as potential indoor environments to perform DAC (iCO_2-DAC). Typical CO_2 concentrations in such spaces, substantially higher than atmospheric concentrations, are reported and discussed, and the different factors contributing to the CO_2 concentration in indoor environments and current mitigation strategies are reviewed. The information provided lays the basis to perform a techno-economic assessment of iCO_2-DAC that is still missing in the literature.

2. Indoor Air Quality

The World Health Organization (WHO) identified exposure to poor air quality (indoors and outdoors) as the most important environmental threat to global public health, with 90% of the world population exposed to air quality below that recommended by WHO guidelines (Health Organization, 2016). While epidemiologic evidence indicates a relationship between outdoor and indoor pollutants (Brunekreef et al., 2005; Yocom, 1982), indoor air pollutants (IAPs) concentrations are higher than outdoor air pollutants (Leung, 2015). IAPs of concern include: particulate matter (PM), biological organisms (fungal spores, bacteria and viruses), allergens, over 400 different chemical compounds, mainly volatile organic compounds (VOCs) such as benzene, toluene, methanol, ethylbenzene and xylene, inorganic compounds (ICs) such as carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x) and ozone (O_3), amongst others (González-Martín et al., 2021; Kraakman et al., 2021; López de León et al., 2019).To understand the effect of IAPs over human health, it is key to characterize and identify the IAPs and quantify the exposure characteristics. The IAP level is determined by the ventilation rate, and by the concentration, magnitude and density of internal sources. Ventilation rates for buildings are normally designed to prevent reaching unhealthy or uncomfortable pollution levels, but it leads to high energy consumption on heating and cooling of building. Therefore, the most efficient IAP reduction strategy begins with an emission reduction on the source, and dilution with external air. However, there is a need for technologies to improve indoor air quality, and many many research efforts are directed to improve physic-chemical pollution abatement and on the use of new tools, such as biotechnologies (Kraakman et al., 2021).

2.1. Sources of Indoor Air Pollutants

Luengas et al. (2015) grouped IAPs sources into four large categories: 1) endogenous sources, which can be permanent (building materials, carpets, paints, varnishes, etc.) (Harb et al., 2018; Katsoyiannis et al., 2012; Kelly and Fussell, 2019) or occasional (furniture, cleaning and disinfection products, cooking, personal care products, tobacco smoke, etc.) (Kaunelienė et al., 2018; Steinemann et al., 2011); 2) human metabolism (Liu et al., 2017; Tang et al., 2016); 3) reaction products in an indoor environment (Nazaroff and Goldstein, 2015; Wells et al., 2017), and 4) infiltration from the outdoor environment. Many studies state that endogenous sources and human activity related emissions are the major sources of IAPs (Gunschera et al., 2013; Tran et al., 2020). Reaction products might play an important role in indoor air chemistry in the presence of gas phase oxidants like O_3, hydroxyl radicals and nitrate radicals (Wells et al., 2017), which most of the time are released as by-products of incomplete oxidation of other IAPs by indoor air treatment technologies (Debono et al., 2017). Such compounds are hardly measurable by conventional methods and tools due to their low concentration (Farmer, 2019). Indoor air pollution from outdoor environment occurs when outdoor-sourced contaminated air enters indoor spaces and combines with indoor pollutants (González-Martín et al., 2021). Outdoor-sourced contaminated air can have both natural and anthropogenic origin, the latter being the predominant source (Chen and Zhao, 2011). It includes automobile emissions (Perry and Gee, 1994), industrial emissions (Tunno et al., 2015) and many combustion processes such as coal burning, (Zhang and Smith, 2007). Residential biomass burning is also one of the major sources of air pollutants, including $PM_{2.5}$ (Shen et al., 2020b). The most relevant IAPs sources and types are summarized in Table 4.

Table 4.
Summary of the main indoor IAP sources in different indoor air spaces (Samet et al., 1987a, 1987b).

Indoor air space	Source	IAP	Type of source	Reference
Home	Smoking	PM and VOCs	Occasional	Vanker et al., 2019
	Woodstoves	PM, CO, CO_2	Occasional	Vicente et al., 2020
	Building materials	VOCs	Permanent	Wang, 2018
	Earth radon	Radioactivity	Permanent	Jassim and Isaifan, 2018)
	Furnishings	VOCs, PM	Permanent	Chang et al., 2019
	Household products	VOCs	Occasional	Zota et al., 2017
	Car exhaust	PM, NO_x, CO, CO_2, VOCs	Occasional	González-Martín et al., 2021
	Human metabolism	CO_2, CO, VOCs, Bioaerosols	Permanent	Douwes et al., 2003
Office	Smoking	PM, VOCs	Occasional	Kaunelienė et al., 2018
	Building materials	VOCs	Permanent	Šeduikyté and Bliüdžius, 2005
	Printers and photocopy machines-	VOCs, PM, O_3	Occasional	Destaillats et al., 2008
	Cleaning products	VOCs,	Occasional	(Paciência et al., 2016)
	Air-conditioning	CO, CO_2, NO_x, VOCs, PM	Permanent	Yu et al., 2009
	Human metabolism	CO_2, CO, VOCs, Bioaerosols	Permanent	Cheng et al., 2012; JG. et al., 2016
Transportation vehicles	Wear metal emissions due to friction between wheels and rails brake pads	PM	Occasional	Aarnio et al., 2005
	Metals vaporization due to sparking	PM	Occasional	Mohsen et al., 2018
	Outdoor air infiltration	PM, CO_2	Occasional	Leung, 2015
	Building materials	VOCs	Permanent	Cao et al., 2019
	Human metabolism	CO_2, CO, VOCs, Bioaerosols	Permanent	Passi et al., 2021
	Chemicals and lubricants	VOCs	Occasional	Shiohara et al., 2005

2.2. Exposure to Indoor Air Pollutants

The second factor influencing the effect of IAPs over human health is the exposure, which is defined as the contact over time and space between a person and one or more biological, chemical or physical agents (National Research Council, 1991). Several methods to assess exposure in human populations have been developed over time (International Programme on Chemical Safety (IPCS), 1993). An exposure assessment requires a complex analysis of different aspects about the contact between people and hazardous substances (International Programme on Chemical Safety (IPCS), 2000). According to Sexton et al. (1995), the most important aspects of exposure analysis, are: 1) agents (biological, chemical, physical, single agent, multiple agent, mixtures), 2) sources (anthropogenic/non-anthropogenic, area/point, stationary/mobile, indoor/outdoor), 3) transport/carrier medium (air, water, soil, dust, food, product/item), 4) exposure pathway (ingestion of food, breathing contaminated air, touching residential surface), 5) exposure concentration units (food-mg/kg, water-mg/liter, air-μg/m^3, contaminated surface-mg/cm^2, weight-%, fibres/m^3-air), 6) exposure route (inhalation, dermal contact, ingestion, multiple routes), 7) exposure duration (seconds, minutes, hours, days, weeks, months, years, lifetime), 8) exposure frequency (continuous, intermittent, cycling, random, rare), 9) exposure setting (occupational/non-occupational, residential/non-residential, indoor/outdoor), 10) exposed population (general population, population subgroups, individuals), 11) geographic scope (site/source specific, local, regional, national, international, global), 12) time frame (past, present, future, trend).

From the aforementioned exposure parameters, the first six are related to the pollutant characteristics and properties and allow estimating the pollutant concentration. The last six are related to the person and the exposure time. Although the concentration of IAPs and the number of carcinogenic air pollutants has decreased since the 1950s (Weschler, 2009), the technological development and the rise of specialized occupational activities have drastically increased the time we spend indoors versus outdoors (Luengas et al., 2017). While we have gained knowledge about IAPs, we currently spend ~80-90% of the time indoors (Boor et al., 2017; N.E. Klepeis et al., 2001). This behaviour increases our exposure to IAPs (Dales et al., 2008; Leech et al., 2002), and their long-term health effects have become more apparent over the last decades, as current building designers prioritize energy savings over IAPs concentrations (González-Martín et al., 2021). Consequently, the scientific community is increasingly investigating the impact of IAPs on human health (Allen et al., 2016; Bernstein et al., 2008; Boor et al., 2017; Erdogan et al., 2012; Seppanen et al., 1999; Tham, 2016; Tran et al., 2020; Zhang et al., 2017a).

2.3. Indoor Air Quality And Human Health

The consequences of bad Indoor Air Quality (IAQ) can be quantified and have been summarized by the WHO (World Health Organization, 2021) as follows: 1) 91% of the global population breathes poor-quality air; 2) about 7 million people die every year due to indoor and outdoor air pollution, mainly from low and middle-income countries; 3) each year, close to 4 million people die prematurely from illness attributable to household air pollution due to the use of solid fuels and kerosene. Moreover, hazardous stoves, source of pollutants such as particulate matter (PM), volatile organic and inorganic compounds (VOCs and VICs, respectively), are commonly used; 4) household air pollution causes non-communicable diseases including strokes (18%), ischaemic heart disease (27%), chronic obstructive pulmonary disease (COPD) (20%) and lung cancer (8%); 5) around 2.6 billion people cook using polluting open fires or simple stoves fueled by kerosene, biomass (wood, animal dung, and crop waste) and coal; 6) 45% of children under the age of 5 who died of pneumonia became ill from IAPs. Household air pollution also contributes to 28% of all adult deaths from pneumonia. Simultaneous exposure to multiple substances is of high relevance in public settings, especially for vulnerable groups such as children, given the co-occurrence of chemicals and the time spent indoors. The latest evidence of the negative health impacts of indoor air pollution in public settings for children was recently reviewed by the WHO (World Health Organization, 2021). A WHO's recent document provides measures to reduce risks for children's health from combined exposure to multiple chemicals in indoor air in public settings for children (World Health Organization, 2022).

The most common health symptoms caused by short-term exposure to IAPs are ocular and respiratory system irritation (eyes, nose, and throat), headaches, dizziness, fatigue and nausea (Paleologos et al., 2021), whereas chronic exposure to IAPs can cause different types of cancer (breast and lungs) (Brody et al., 2007; Pershagen, 1990), asthma (Rumchev, 2004), cardiovascular diseases (Tran et al., 2020), damage to the liver (Kim et al., 2014), kidneys (Afsar et al., 2019), reproductive system (Veras et al., 2010), endocrine system (Rudel and Perovich, 2009) and central nervous system (Kim et al., 2020). Nowadays, there is a solid body of scientific evidence that correlates IAPs and all the above-mentioned health symptoms and diseases. Nonetheless, affection to the respiratory system is the most important among the disorders associated with bad IAQ, since inhalation is the major exposure route for IAPs (Hulin et al., 2012).

Besides acute health symptoms, IAPs can also affect the cognitive performance of office workers (Allen et al., 2016; Zhang et al., 2017b). A cognitive and physical performance degradation occurs when PM, VOCs and CO_2 accumulates in indoor air spaces with limited air renovation (Allen et al., 2016; Zhang et al., 2017b). A cognitive performance study followed 302 office workers in 6 countries for a year and observed a 0.8-0.9% slower response times for every 10 $\mu g/m^3$ increase in $PM_{2.5}$, and 1.4-1.8% slower response times for every 500 ppm_v increase in CO_2 (Cedeño Laurent et al., 2021).

2.4. Indoor Air Pollutants

IAPs can be divided in four groups (Gibson et al., 2019): 1) radon; 2) VOCs (alkanes, formaldehyde, esters, ketones and aromatic organic compounds); 3) biological organisms (fungal spores, bacteria and viruses) and allergens (pollens, moulds, mites, insects); 4) combustion and Environmental Tobacco Smoke (ETS) products (PM, wood/coal smoke, CO_x, NO_x, SO_x). The main compounds found in indoor air can be divided according to their chemical nature: 1) VOCs, 2) Biological contaminants, 3) Particulate matter and 4) Inorganic gaseous pollutants. The main pollutants of each class are described in this section. Further information about IAPs is gathered in the WHO guidelines (World Health Organization, 2010).

2.4.1. Biological Contaminants: Organisms and Allergens

Biological contaminants can be divided into two categories: organisms and allergens (Dales et al., 2008). Besides, the US EPA introduced the concept of airborne biological pollutants (ABPs), which include: 1) pollens, which originate from plants, 2) viruses, which are transmitted by people and animals, 3) mold, 4) bacteria, which are carried by people, animals, and soil and plant debris, 5) skin flakes, dander and saliva of household pets, 6) dropping and body parts of cockroaches, rodents and other pests and insects, 7) proteins in urine from rats and mice, 8) mold, mildew and other sources of biological contaminants from contaminated central air handling systems (US EPA, 2021b). Although most ABPs sources are domestic (Fan et al., 2021; Rosa et al., 2013), they can be found in a large variety of indoor environments such as offices (Reynolds et al., 2016; Wolkoff et al., 2021), and transportation vehicles (Passi et al., 2021; Xu and Hao, 2017).

ABPs can affect human health by a variety of biological mechanisms including infections from rhinitis (Lemanske, 2003), inflammations such as alveolitis, atopic dermatitis, allergies such as contact urticaria and pseud-allergic and hypersensitivity reactions such as atopic eczema (Michel et al., 2022).

The COVID-19 pandemic has further highlighted the importance of IAQ, since the disease is mainly transmitted through respiratory aerosols (Greenhalgh et al., 2021) just like other respiratory diseases (Wang et al., 2021). The Healthcare Infection Control Practices Advisory Committee (HICPAC) suggested that a person can become infected at long distances from the contagious person by airborne/aerosol transmission (Jones and Brosseau, 2015; Siegel et al., 2007).

A threshold between respiratory aerosols and droplets has been indicated at an aerodynamic diameter of 100 μm, considering the transport phenomena and exposure routes (inhalation for aerosols *vs.* impaction for droplets) (Prather et al., 2020; Tang et al., 2021). For COVID-19, it has been estimated that the risk of transmission in indoor spaces is 19 times higher than outdoors (Bulfone et al., 2021), which can only be explained by aerosol transmission due to poorly ventilated spaces, increasing the amount of virus being inhaled by the susceptible population (Tang et al., 2021). As shown in Figure 2, without sufficient ventilation with outdoor air or mechanical air filtration, aerosols containing respiratory pathogens from an infected individual will accumulate and remain airborne for minutes to hours. Such conditions increase the probability of respiratory disease transmission, which can be mitigated using high efficiency filtration masks, ventilating with outdoor air, and increasing the mechanical filtration efficiency of air in indoor spaces.

Historically, many pathogens were considered only transmissible through ballistic droplets and later known to be transmissible through aerosols, e.g. measles (Riley et al., 1978; Riley, 1982), SARS (Yu et al., 2004), MERS (Kim et al., 2016), influenza (Cowling et al., 2013; Tellier, 2009) and most recently SARS-CoV-2 (Greenhalgh et al., 2021; Tang et al., 2021). To avoid repeating this mistake and prevent respiratory disease transmission, the IAQ must be improved, similarly to how enteric diseases have been reduced through safe drinking water and sanitation services (Brown et al., 2013).

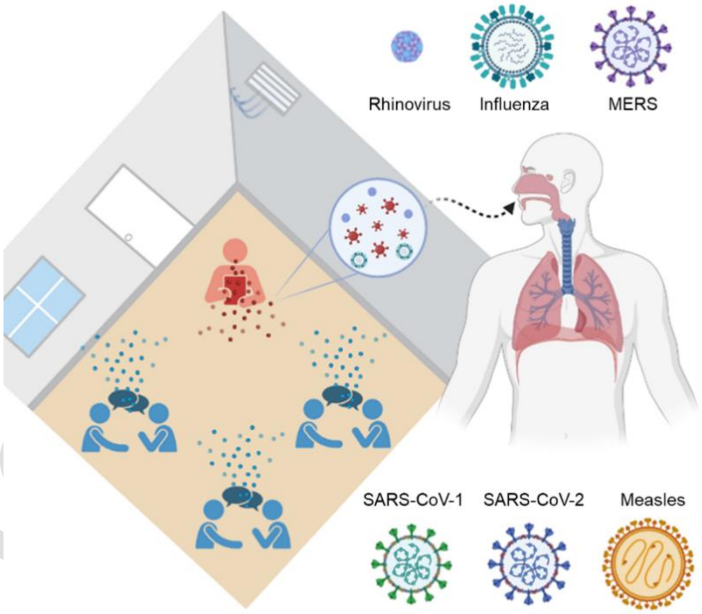


Fig. 2. Graphical representation of aerosol transmission of respiratory diseases in a room. Figure created with Biorender.

2.4.2. Volatile organic compounds

VOCs have been related to a large spectrum of illnesses ranging from mild such as irritations (Chen et al., 2005) to very severe diseases such as cancer (Manisalidis et al., 2020) . The main VOCs found in indoor air environments are benzene, toluene, xylenes and aldehydes (formaldehyde and acetaldehyde) which should be considered priority pollutants due to their health effects (Harb et al., 2018). Formaldehyde (HCHO) is the most familiar VOC in indoor air pollution, since its major sources are indoor construction materials such as particleboard, fiberboard and plywood. The concentration of formaldehyde is much higher in residential buildings compared with office buildings because of the large ratio of pressed wood products to air volumes in homes (Bernstein et al., 2008).

Among the most common aromatic organic compounds found in indoor air environments, benzene is the one with the major health risk. Benzene is a carcinogenic compound via genotoxic mechanism in humans (Becerra et al., 2020) and no safe level of exposure are recommended (World Health Organization, 2010). Both the acute, non-carcinogenic effects of exposure to high concentrations of benzene and the carcinogenic effects of long-term exposure to lower concentrations have been widely investigated (Duarte-Davidson et al., 2001; Garcia-Jares et al., 2019; Kodavanti et al., 2015). Although benzene is mainly generated outdoors by the transport sector (combustion of fossil fuels), it is also found indoor due to outdoor air intrusion. Indoor sources include combustion events (heating, cooking, smoking, etc.), building materials, furniture, and solvents among others (Kaunelienė et al., 2018; Sarkhosh et al., 2021).

Another relevant organic aromatic compound found in indoor air environments is toluene, an aromatic alkylbenzene hydrocarbon present in many commercial products, including adhesives, paint thinners, and cleaning agents (Low et al., 1988; Meek et al., 1994; Win-Shwe and Fujimaki, 2010). Toluene is one of the main additives of unleaded gasoline, containing up to 35 % of toluene by volume (Vulimiri et al., 2017). Due to its chemical structure, toluene is highly lipid soluble, therefore it readily crosses the blood-brain barrier and has an affinity for white matter (Eicher, 2009). Similarly to benzene, intrusion of outdoor air containing toluene is one of the major toluene sources in indoor environments including home/office environments (Poza-Casado et al., 2021; Rosário Filho et al., 2021; Shrestha et al., 2019) and underground transportation vehicles (Cao et al., 2019; Elsaid and Ahmed, 2021), especially those based on fossil fuels (Chiu et al., 2015; Perry and Gee, 1994).

2.4.3 Particulate matter pollution

Particulate matter (PM) pollution includes particles with diameters of 10 μm or smaller, called PM_{10}, and fine particles with diameters around 2.5 μm, called $PM_{2.5}$ (Manisalidis et al., 2020).. Some authors divide

PM into several categories, according to the type and size (Heal et al., 2012): smog, soot, tobacco smoke, fly ash, biological contaminants and types of dust (atmospheric, heavy and settling dust). Environmental Tobacco Smoke (ETS) products are a major source of PM in places where is allowed to smoke inside, accounting for as much as 50-90% of the total indoor PM concentration (World Health Organization, 2010). Early studies about ETS exposure (Öberg et al., 2011), revealed that almost half of the world´s children (40%) are regularly exposed to ETS followed by non-smoking women (35%) and men (33%). An ambient $PM_{2.5}$ increase of 10 $\mu g/m^3$ has been associated with 15-27% increased risk of lung cancer mortality in a cohort study that followed 188,699 lifelong never-smokers from 1982 to 2008 (Turner et al., 2011). Most of ETS and combustion products are present in home environments, but some of them, such as PM and $CO_{2,}$ are also largely present in office environments (Cheng, 2017; Zhang et al., 2020), schools (Becerra et al., 2020; Janssen et al., 2001) and transportation vehicles (Aarnio et al., 2005; Cheng et al., 2012; Kam et al., 2011). A strong correlation of respiratory symptoms, such as lung function reduction, bronchial hyperresponsiveness, asthma and COPD, with high concentrations of ETS and other combustion products such as PM in indoor environments frequented by smokers has been established by several authors (Samet et al., 1987a, 1987b; Wolkoff, 2018). Further information regarding the association between PM and adverse health effects can be found elsewhere (Kelly and Fussell, 2012).

2.4.4 CO_2 and other inorganic gases

Inorganic gas pollutants found in indoor air include, among others, CO_2, CO, SO_2, NO_2, O_3, radon (Rd) and acidic gases such as HCl and HNO_3 arising from outdoor-to-indoor transport and thermal decomposition of PVC (Zhang and Smith, 2003). The presence of these gases in urban outdoor environments has gained attention due to increasing traffic and industrial emissions, while its infiltration and accumulation in indoor air causes exposition to building occupants. The concentration of pollutants such as CO, NO_2 and SO_2 has been monitored in schools, where there are not internal sources of such gases (Blondeau et al., 2005; Lee and Chang, 2000; Rivas et al., 2014), concluding that indoor concentration depended on the surrounding emissions, traffic intensity, seasonality, ventilation and buildings permeability. On the other side, combustion in gas stoves and woodstoves are the principal source of CO, SO_2 and NO_2 in households(Seals and Krasner, 2020; Vicente et al., 2020). Unappropriated combustion and the use of improperly operated and maintained appliances is the leading cause of CO poisoning, which occurs due to a strong binding between haemoglobin and CO that can cause death (Zhang and Smith, 2003). Indoor NO_2 exposure is associated to high temperature combustion on gas stoves, and constitutes a higher risk factor for respiratory illnesses compared with electric stoves (Basu and Samet, 1999).

Ozone is a strong oxidizing agent that can be generated by photocopies and laser printers (Destaillats et al., 2008), as a by-product of the electro-photographic process. It causes breathing problems and irritate mucous membranes, reduce lung function, exacerbate asthma, irritate eyes and nose, reduce resistance to colds and other infections and speed up ageing of lung tissue (Mendell and Heath, 2005; Zhang and Smith, 2003). Furthermore, it reacts with other volatile compounds to form contaminant by-products (Nazaroff and Goldstein, 2015; Wells et al., 2017).

Radon, one of the major concerning IAPs, is a naturally occurring radioactive gas which can be found in soils, rocks and water (Leung, 2015; Thang et al., 1995). In outdoor air, it is not considered a threat to public health because it is quickly diluted in the atmosphere (Bowie and Bowie, 1991; Vogiannis and Nikolopoulos, 2015). However, it accumulates in closed environments with poor ventilation through cracks and holes in the foundation and some studies consider building materials an important source of radon in indoor environments (Dales et al., 2008; Denman et al., 2007). Exposure to radon isotopes is the second most important cause of lung cancer in many countries (Petersen and Larsen, 2006). A recent study indicates that in 2018 there were 226,057 radon-attributable lung cancer deaths in 66 countries (Gaskin et al., 2018).

Indoor CO_2 comes primarily from combustion reactions during household activities such as cooking (Shen et al., 2018), heating (Shen et al., 2020b), smoking (Baker, 1983) and from human metabolism (Shen et al., 2020a). Metabolic CO_2 release by respiration has a major impact on the overall CO_2 concentration in office environments and transportation vehicles. The next sections will focus on CO_2, discussing in details its concentration in indoor environments and proposing potential solutions to improve IAQ avoiding health effects attributable to its accumulation in indoor spaces.

3. Potential of Indoor CO_2 Direct Air Capture (iCO_2-DAC) as renewable carbon feedstock

This section gives insights on CO_2 concentration in indoor air and the causes and consequences of its accumulation. Furthermore, the potential of performing indoor CO_2 Direct air capture (iCO_2-DAC) in these environments is explored. Performing iCO_2-DAC in indoor environments would contribute to human health by improving IAQ and reduce the energy expenses of cooling and heating the spaces for occupant's comfort.

3.1. Health effects of CO_2 accumulation

CO_2 is a product of cellular metabolism generated during the Krebs cycle, which takes place in the mitochondria (Huttmann et al., 2014; Osellame et al., 2012). CO_2 enters the bloodstream by diffusion, eventually reaches the pulmonary capillaries by convection and then diffuses through the alveolar membrane into the alveoli, where it can be eliminated via the airways (Patel et al., 2021). The driving force for the diffusion is the partial pressure of CO_2 (P_{CO2}) difference between the alveolar spaces (about 40 mm Hg) and the blood in the pulmonary capillary (about 46 mm Hg) (DuBois et al., 1952), which ensures CO_2 exchange within the alveolar spaces and the blood (Huttmann et al., 2014), as shown in Figure 3(A). When a ventilation failure occurs, or an excess of CO_2 is inhaled, as shown in figure 3(B), an elevation of CO_2 concentration in the bloodstream occurs, i.e., hypercapnia, causing respiratory acidosis (Patel and Sharma, 2021). Hypercapnia can be caused by CO_2 manipulation (dry ice, food and floral preservation), closed and restrained environments (spacecraft, submarines), pathology (pulmonary diseases, sleep apnea), and combustion gas inhalation (tobacco smoke, vehicles) (Guais et al., 2011).

Depending on the exposure time, the maximum acceptable CO_2 concentration in healthy environments varies between 500-3,000 ppm_v (Guais et al., 2011). Respiratory acidosis in healthy adults with a moderate physical load occurs when exposed to CO_2 concentration above 10,000 ppm_v for at least 30 min (Azuma et al., 2018). Respiratory acidosis is a consequence of hypercapnia as the results of the increase of bicarbonate content in blood, which decreases the pH below 7.4 (Cunningham et al., 1986). Depending on the CO_2

concentration, other pathologies can appear. Figure 4 summarizes the guideline values of CO_2 concentration in indoor environments and the different health effects related to such concentrations.

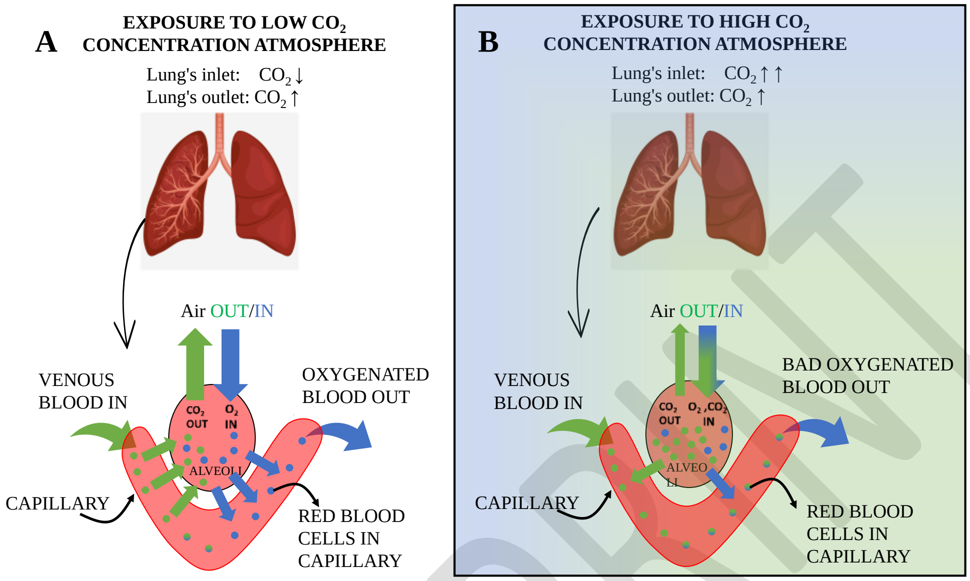


Fig. 3. Diagram showing the carbon dioxide exchange inside the lungs during the A) exposure to a low CO_2 concentration atmosphere and B) exposure to high CO_2 concentration atmosphere.

Cellular metabolism can be affected when exposed to CO_2 concentrations between 10,000 and 50,000 ppm_v causing enhanced glycolysis and reduction of respiration (Goldsmith and Narvaez, 1975; Shirlaw, 1931). Exposure to CO_2 concentration from 100,000 and 300,000 ppm_v (10 to 30%) lead to respiratory function failure with loss of consciousness (Herren et al., 2017), while symptoms of paralysis are shown over 85,000 ppm, whereas death occurs within a short time over 200,000 ppm (Guais et al., 2011). Zhang et al. (2017a) reviewed the effects of exposure to elevated levels of CO_2 (50,000 to 150,000 ppm_v) for relatively short time (less than 1 hour), reporting an increase in respiration rate, minute ventilation rate, and end-tidal CO_2 ($ETCO_2$) (Zhang et al., 2017a).Long exposure (days to months) to low CO_2 levels (5,000 to 15,000 ppm_v) were reported to cause physiological responses such as increased respiratory minute ventilation rate, $ETCO_2$, acidosis and reduced cerebral blood flow (Gortner et al., 1971; Sliwka et al., 1998). However, since CO_2 concentration increased along the time due to the metabolically generated CO_2 and the lack of outdoor air supply, the observed physiological changes and subjective responses could not be attributed only to CO_2 but also to other human bioeffluents (Zhang et al., 2017a).

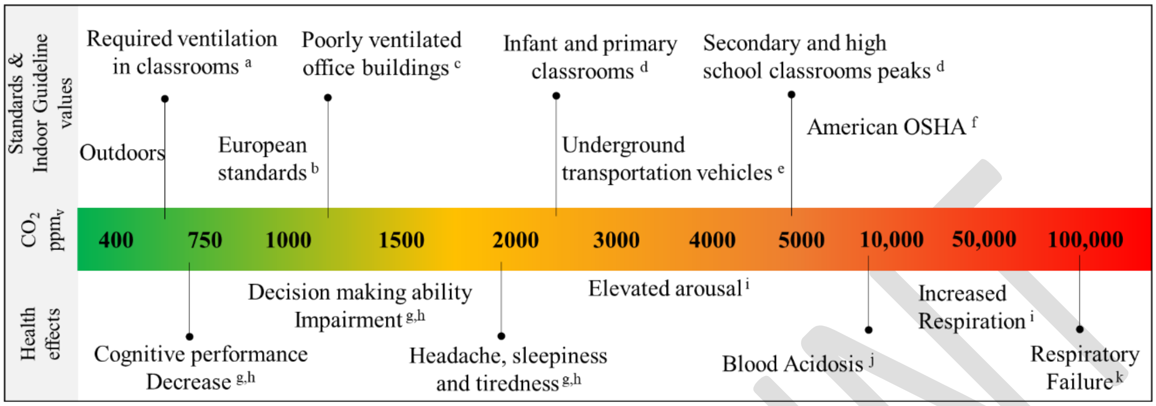


Fig. 4. Correlating chart of the Standards and Indoor Air Guideline values for CO_2 and health effects of CO_2 exposure according to a: Kephalopoulos et al. (2014); b: EN 13779, 2008; c: Le Quéré et al. (2019); d: Becerra et al. (2020); e: Gao et al. (2019); f: OSHA, 1987; g: Satish et al. (2012); h: Allen et al. (2016); i: Zhang et al. (2017b); j: Azuma et al. (2018); k: Guais et al. (2011).

In other experiments, subjects were exposed to 3,000 ppm_v for 2-3 hours (Kajtár and Herczeg, 2012), to 1,000 to 2,500 ppm_v (Satish et al., 2012), and up-to 1,400 ppm_v for 8 hours (Allen et al., 2016). Besides some physiological effects such as diastolic blood pressure, all three studies exhibited a similar pattern, with a significant decrease of cognitive function and decision-making ability for CO_2 levels of 945-1,400 ppm_v. Furthermore, exposure to CO_2 concentrations above 2,000- 3,000 ppm_v, along with other bioeffluents, may elevate arousal or cause health symptoms (headache, sleepiness, tiredness) which reduce the cognitive performance. Such symptoms correlate with hypercapnia, suggesting that when the CO_2-rich blood reaches the brain, the chemoreceptors detect the changes in the pH and bicarbonate content in the blood, affecting brain functioning (Shriram et al., 2019). Therefore, there is strong need to monitor and control indoor CO_2 concentration to avoid acute and chronic health effects and cognitive performance degradation.

3.2. CO_2 as an IAQ metric

Due to the inherent relation between human occupancy and CO_2 concentration in indoor environments, CO_2 concentration has been used as an indicator for IAQ (Olesen et al., 2020). Moreover, since indoor CO_2

concentrations are always accompanied by other pollutants emitted by humans (humans bioeffluents) or by buildings, indoor CO_2 concentrations can be used to estimate the concentration of other pollutants, and determine the proper ventilation rate (Azuma et al., 2018; Seppanen et al., 1999). However, CO_2 itself can be considered as an indoor pollutant, and not simply as a surrogate for other bioeffluents and indoor pollutants (Allen et al., 2016; Kajtár and Herczeg, 2012; Satish et al., 2012).

Several regulations and standards establish the acceptable CO_2 concentration levels to design ventilation systems in buildings (Schibuola and Tambani, 2020). Becerra et al. (2020) summarized the different European standards and National building regulations, and reported long-term health-based indoor air guideline values (IAGVs) for CO_2. The minimum IAGVs reported is 800 ppm_v and corresponds to the European Standard EN 13779 from 2008 (13779, 2008). This is slightly more restrictive than national regulations such as the French (Reglement sanitaire departemental type (RSDT), J. Officiel. Repub. Fr., 1978), Portuguese (Portaria n. 353-A/2013, 2013) and United Kingdom regulations (ESFA, 2016), which set an average IAGVs of 1,000 ppm_v for non-smoking and non-residential buildings, 1250 ppm_v during room occupancy and 1,000 ppm_v during occupancy with mechanical ventilation, respectively. American standards, for example the Occupational Safety and Health Administration (OSHA) has established a Permissible Exposure Limit (PEL) for CO_2 of 5000 ppm_v (0.5% CO_2 in air) averaged over an 8-hour work day (OSHA, 1987). Similarly, the American Conferences of Governmental Industrial Hygienists (ACGIH) (ACGIH, 1991) set a threshold limit value (TLV) of 5000 ppm_v and a top exposure limit of 30,000 ppm_v for a 10-minute period . On the other hand, the American Society of Heating defined 1,000 ppm_v as a criterion for defining good IAQ, similar to the European standards.

Although many researches relied on the threshold provided by the ACGIH, others have questioned the TLV values of over 142 substances provided because they lack of consistency and transparency (Smith and Perfetti, 2019). Although CO_2 was not considered within the 142 substances studied by Smith and Perfetti, their study highlights the importance of taking into account the considerations built around the TLV's values reported in the literature.

The American Refrigerating and Air-Conditioning Engineers (ASHRAE) 62.1 standard has not limited the indoor CO_2 concentration for the past 30 years (Persily, 2020). However, as thoroughly explained by Persily (2020), the confusion regarding CO_2 in Standard 62.1 is likely associated to an informative appendix to explain the connection between outdoor air ventilation rates and steady-state levels of CO_2 per person. According to this standard appendix (ASHRAE, 2018), for the CO_2 generation rate of 0.3 L/min, typical of a sedentary person, 7.5 L/s of outdoor air are needed to dilute odours from human bioeffluents to levels that will satisfy about 80% of visitors.

3.3. CO_2 concentration for representative indoor air environments

Most studies report that indoor CO_2 concentration in occupied spaces is commonly below 2,500 - 3,000 ppm_v (Bekö et al., 2010; Hwang et al., 2017a; Santamouris et al., 2008; Satish et al., 2012; Seppanen et al., 1999; Shen et al., 2020a), although it can reach as high as 4,000-5,000 ppm_v (Becerra et al., 2020; Chiu et al., 2015; Park and Ha, 2008; Zhang et al., 2017a). There is high heterogeneity in the concentrations observed in indoor spaces, which mainly depend on the occupancy and the type of activities being conducted. In this review, three representative indoor environments are studied: school, office and underground public transportation vehicles. These three spaces have been selected as representative indoor spaces for the range of CO_2 concentrations that can be found, from school classrooms that tend to have low to mild CO_2 concentration, office environment with mild CO_2 concentration to underground public transportation vehicles with the highest CO_2 concentrations in indoor environments. There are other indoor environments of interest that could be further studied such as shopping centres, public buildings, indoor sports facilities and house environment, that are out of the scope of this work.

3.3.1. School environment

Due to the observed health effects of increased CO_2 concentrations in enclosed spaces, several studies have been conducted in infant, primary, middle and high schools, where students spend several hours (Choe et al., 2022; Di Gilio et al., 2021; Gil-Baez et al., 2021; Mohamed et al., 2021; Zhu et al., 2021). A recent study reported that, in Spain, all the classrooms under investigation had short-term periods with CO_2

concentrations above all IAGVs (European, French, Portuguese and U.K IAGVs) with peaks of 3,284 ppm_v for the infant and primary classrooms, and 5,366 ppm_v for secondary and high schools (Becerra et al., 2020). Becerra et al. (2020) correlated these values with ventilation and occupancy rate, which was as low as 2.5 m^2/student for secondary schools and high schools, resulting in high mean CO_2 concentrations. A similar study in Germany evaluated indoor air quality in 64 schools, obtaining a median CO_2 concentration of 1,603 ppm_v in the winter and 405 ppm_v in summer, which highlights the importance of climate parameters due to different ventilation practices (Fromme et al., 2007). The average CO_2 concentration reported by the European SINPHONIE investigation project was 1581 ppm_v while values up to 3530 and 4960 ppm_v are reported as peak concentration reached in kindergartens and primary schools (Regional Enviornmental Center, 2014). These studies raise the attention on the importance of risk reduction measures towards the minimization of CO_2 concentration within classrooms. Recent studies demonstrated the link between IAPs, including CO_2 and acute health effects as well as impairment of cognitive development and learning performance within schoolchildren's (Kotlík et al., 2022; Szabados et al., 2021).

To ensure the well-being conditions for the students and enhance their learning process and cognitive performance, as well for health reasons (Andualem et al., 2019; Cornaro et al., 2013; Poza-Casado et al., 2021; Stabile et al., 2016), the guidelines for healthy environments within European Schools present a subset of indicators and protocols that have been adjusted to the objectives of WHO to monitor IAPs (Kephalopoulos et al., 2014).

Ventilation by the infiltration of outdoor air is the technique used to reduce CO_2 accumulation. Nowadays, in European Schools, the ventilation rate is expressed as L/s per person and no longer simply as air changes per hour (ACH), thereby taking into account the occupancy density of the school room. According to the guidelines for healthy environments within European Schools (Kephalopoulos et al., 2014), when natural ventilation is used, CO_2 levels above 1,500 ppm_v should be avoided. Additionally, classrooms should be equipped with CO_2 monitor alarms that signal when the CO_2 level exceeds 700 ppm_v, requiring ventilation.

In the UK, according to the education and skills funding agency (ESFA, 2016), when mechanical ventilation or hybrid systems operated in mechanical moderate use, sufficient outdoor air should be provided to maintain the daily average CO_2 concentration to less than 1000 ppm_v during the occupied period, while in teaching and learning spaces with natural ventilation or hybrid systems operated in natural mode, a daily average CO_2 concentration below 1,500 ppm_v should be maintained. Furthermore, 1,500 ppm_v should not be exceeded for more than 20 consecutive minutes. In the US, based on the IAQ tools for schools developed by the EPA (EPA, 2009), CO_2 concentrations in schools should comply with the ASHRAE standard 62-2001 limit of 700 ppm_v above the outdoor concentration (slightly above 1,000 ppm_v in total) (ASHRAE Standard 62-2001, 2001).

Santamouris et al. (2008) compared the efficiency of natural ventilation by window opening with mechanically ventilated schools in Athens (Greece). The study included 287 classrooms from 182 schools with natural ventilation, and only 25% of them presented average CO_2 concentrations lower than 1,000 ppm_v, with 47% higher than 1,500 ppm_v, and 18% higher than 2000 ppm_v. On the other hand, from the 900 classrooms studied from 220 schools with mechanical ventilation, 52% had average indoor CO_2 concentration below 1.000 ppm_v, 15% over 1,500 ppm_v and 5% above 2,000 ppm_v. Although mechanical ventilation reduces indoor CO_2 concentrations, there is still a large margin of improvement in order to lower CO_2 concentrations below the reference values. A review study highlighted that schools generally have low ventilation rates, resulting in CO_2 concentrations above 1,000 ppm_v (Fisk, 2017). A research study carried out in a middle school in Rome (Italy) evaluated the effectiveness of ventilation rates of a natural trickle ventilation system though an interactive approach involving the pupils, that was set to increase air exchange when a threshold limit of 1.000 ppm_v was reached (Cornaro et al., 2013). However, the long-term monitoring campaign showed that the average indoor CO_2 concentration exceeded the 1,500 ppm_v value referenced from ESFA, demonstrating that the system was not able to fulfil its performance requirements.

These observations suggest that schools would benefit from increased ventilation with outdoor air, or CO_2 removal through engineered solutions. However, most schools often face budgetary and maintenance staff shortages, which can result in poor IAQ (Shaughnessy et al., 2006).

3.3.2. Office indoor environment

Despite having a ventilation system, the indoor CO_2 concentration in offices is often between two or three times the atmospheric CO_2 concentration of 407.8 ±0.1 ppm_v (Le Quéré et al., 2019). Guidelines in many European countries (Finland, Norway, Sweden, Denmark) recommend that the CO_2 concentration in offices should not exceed 1,000 ppm_v (Küçükhüseyin, 2021). An IAGV of 1.000 ppm_v is provided in the French regulation (Reglement sanitaire departemental type, RSDT). J. Officiel. Repub. Fr., 1978), with a tolerance of 1,300 ppm_v in non-smoking and non-residential buildings (offices). Similarly, in South Korea, the CO_2 concentration must be kept below 1,000 ppm in office buildings (Hong et al., 2018). In Germany, a value of 1,500 ppm_v applies as a hygienic guide value according to DIN 1946 part 2 (Fitzner, 1993). In the US, many local building codes use the ASHRAE standard of 20 cfm/person (10 L/s per person), which corresponds to an indoor CO_2 concentration of 945 ppm_v (Allen et al., 2016). Indoor CO_2 concentration within office buildings in the US is also regulated by the OSHA standard for CO_2 of 5,000 ppm_v (0.5% CO_2 in air) averaged over an 8-hour work day (time-weighted average-TWA) (OSHA, 1987) or the ACGIH guideline that suggests a TLV of 5,000 ppm_v (ACGIH, 1991). However, some local IAGV within the USA are much more stringent, like the Massachusetts Department of Public Health (MDPH) that uses a guideline of 800 ppm_v for occupied buildings (Burge and Hoyer, 1990; Gold, 1992). Hence in summary, with the exception of the OSHA guideline, the indoor CO_2 concentration set as acceptable level for office indoor environment is below 1,000 ppm_v and unacceptable CO_2 concentration level is above 2,000 ppm_v (Hong et al., 2018). Research on indoor CO_2 concentration in offices is strongly associated to the study of building related symptoms (BRS), also called sick building syndrome (SBS), defined as a set of symptoms with unidentified etiology frequently reported by building occupants, especially in office buildings (Apte et al., 2000; Erdmann and Apte, 2004; Erdmann et al., 2002; Sarkhosh et al., 2021; Seppanen et al., 1999). SBS symptoms are associated with occupancy in buildings and decrease when the individuals are absent from the building (Seppanen et al., 1999). According to the WHO working group (World Health Organization, 1983) SBS is characterized by eye, nose and throat irritation, a sensation of dry mucous membranes and skin, mental fatigue, headache, a high frequency of airway infections and cough, nausea and dizziness.

Within SBS symptoms, special attention has been placed towards the effects of CO_2 on human decision-making performance (Bakó-Biró et al., 2012; Satish et al., 2012; Šeduikyté and Bliüdžius, 2005). According to Seppänen (2007), the effect of ventilation on health and productivity can be summarized into the following 5 points: 1) higher ventilation reduce the prevalence of airborne infectious diseases; 2) ventilation rates below 10 L/s per person are associated with a significantly worse prevalence of one or more health concerns or perceived air quality outcomes; 3) ventilation rates above 10 L/s per person, up to 20 L/s per person, are associated with a significant decrease in the prevalence of SBS symptoms; 4) improved ventilation can improve task performance and productivity and 5) ventilation rates below 0.5 Air Changes per Hour (ACH) are a health risk in Nordic residential buildings. Relative to natural ventilation, air conditioning is often associated with statistically significant increase in the prevalence of one or more SBS symptoms.

Several studies found strong association between CO_2 concentration, ventilation rates and health in office buildings (Apte et al., 2000; Zhang et al., 2017a). In this sense, Seppänen et al. (1999), found a positive correlation between CO_2 levels and one or more SBS symptoms in half of the 22 studies considered, where CO_2 concentration measurements were made over 30,000 subjects in more than 400 buildings in North America, Europe, and Asia. They concluded that the risk of SBS symptoms decreases with CO_2 concentration below 800 ppm_v. Apte et al. (1996) found statistically significant dose-response relationships between the indoor and outdoor CO_2 level difference (dCO_2), and SBS symptoms with odds ratios ranging from 1.1 to 1.5 per 100 ppm increase in dCO_2 levels (Apte et al., 2000). The odds ratio is defined as a measure of association between an exposure and an outcome, being OR>1 an exposure associated with higher odds of outcome and OR<1 an exposure associated with lower odds of outcome (Sedgwick and Marston, 2010). These findings suggest that CO_2 levels in office spaces should be kept as close to outdoor concentrations as possible. This statement is supported by Erdmann and Apte (2004), who demonstrated that in the most ventilated buildings (lowest dCO_2) SBS symptoms were reduced by a maximum of 64-85% depending on the symptom, compared to buildings that just meet the ASHRAE minimum ventilation standard.

The introduction of fresh air increases the comfort of the occupants and serves to dilute normally occurring environmental pollutants. However, according to Seppänen (2007), proper ventilation methods are important for the total energy efficiency of office buildings. In order to choose the most energy efficient and healthy ventilation system, factors such as climate conditions, building type and occupant behaviour pattern and expectations should be considered (Kim and De Dear, 2012). Mechanical ventilation system is extensively used in buildings in hot climate (Al Horr et al., 2016). A study conducted in Taipei City (Cheng, 2017) demonstrated that mechanical ventilation resulted in comfortable CO_2 concentrations and room temperatures in agreement with the Taiwan EPA. Indoor CO_2 concentrations in the building were maintained between 450 ppm_v to 750-850 ppm_v during working hours. On the other hand, bare natural ventilation by means of window-opening often lead to unhealthy levels of indoor pollutants and excessive energy loss (Poza-Casado et al., 2021). However, natural ventilation system by means of window opening is an energy-saving and environmentally friendly solution to improve ventilate indoor environments in office environments (Brambilla et al., 2018; Kyritsi and Michael, 2020). Nevertheless, poorly designed natural ventilation can become source of pollutants and allergens of outdoor or indoor origin, elevating the exposure and increasing the health risk instead of decreasing it (Wolkoff et al., 2021). Exposure to outdoor pollutants is not only related to natural ventilation, but most mechanical ventilation systems include efficient filtration and/or air cleaning systems to reduce the exposure to outdoor pollutants (Asikainen et al., 2016). Some studies indicated that mixed mode ventilation systems often offer a good balance of air quality satisfaction and energy savings (Ezzeldin and Rees, 2013; Gou et al., 2014). The Center for the Building Performance Diagnostics at Carnegie Mellon University performed a literature review on the relationship between the work environment and workers productivity (Gou et al., 2014), showing that replacing or supplementing mechanical ventilation with mixed mode conditioning could result in 3–18% productivity gains due to improved thermal comfort and air quality (Vivian Loftness et al., 2005).

A recent investigation focused on the influence of environmental variables on user's thermal comfort and air quality perception in humid subtropical climate (Florianopolis, a southern region of Brazil) (de Oliveira et al., 2021). Researchers compared data from one building with central air-conditioning system and three mixed-mode buildings, in which users could switch between natural and mechanical ventilation mode. Indoor CO_2 concentration varied between 400 and 900 ppm_v in the buildings operated in natural mode, between 400 and 1,300 ppm_v when operated in air-conditioning mode in mixed-mode buildings, and between 400 and 800 ppm_v in the buildings with centralized air-conditioning. Thus, buildings operated in mixed mode could not maintain the CO_2 indoor concentration below the recommended limit (1,000 ppm_v), while buildings operating mechanical ventilation did. Mixed-mode ventilation is a trade-off strategy, allowing energy savings by reducing air-conditioning usage via natural ventilation to decrease CO_2 concentrations.

3.3.3. Underground transportation vehicles environment

Public transportation vehicles, *e.g.* underground metro systems, have rapidly developed worldwide due to the growing demand of green transportation and sustainable development (Xu and Hao, 2017). Underground metro systems account for the majority of the public transportation in many metropolitan cities. For example, in terms of passengers per kilometer, underground transportation accounts for 48% of public transportation in Paris agglomeration, much more than buses (19%) or trains (33%) (Prud'homme et al., 2012), being this number even larger in the Paris municipality (around 80%). In 2020, underground metro system offer accounted for 84% of the total Transports Metropolitans de Barcelona (TMB) network of 20,614,34 passengers per kilometer (Transports Metropolitans de Barcelona (TMB), 2021). This was translated into an annual demand of 217.93 million underground metro trips, accounting for 65% of the total TMB network, while bus trips accounted for 35%, indicating that underground metro system was the preferred transport mode for Barcelona citizens.

In the metropolitan area of London, underground journeys represented a 32.7% of the total transports from January 2011 to May 2021, whereas bus journeys accounted for 59.2% (41,001 million journeys) (Transports forLondon, 2021). The global number of underground metro systems commuters continuously increased over recent years in metropolitan cities. In 2017, the 182 metro systems in the world accounted for a total annual ridership of 53,768 million commuters, with an annual grow rate of 8,716 million commuters in the last six years (+19.5%) (The UITP Observatory of Automated Metros, 2018). Shanghai, a prosperous and densely populated city with one of the largest urban underground metro systems in the world, averaged 8 million daily commuters in 2014, 10.3 million in April 2015 (Gong et al., 2017) and surpassed 11.3 million in March 2017 (Xu and Hao, 2017). Similarly, the subway system of Mexico City, one of the largest megacities in the world with roughly 20 million people, had 4.2 million commuters traveling daily in 2016, almost 21% of the total population (Mugica-Álvarez et al., 2012). This pattern can be extrapolated to many cities of different sizes in order to understand the importance of underground metro systems. Figure 5 summarizes the passenger flow for different cities. Several studies report that commuters spend between 20 to 40 minutes in one day inside the metro wagons (Querol et al., 2012; Xu and Hao, 2017) and about 10 to 20 minutes inside stations (Park and Ha, 2008; Wen et al., 2020). During this time, commuters are exposed to harmful IAPs that can lead to health problems (Loxham and Nieuwenhuijsen, 2019; Triadó-Margarit et al., 2017; Wen et al., 2020).

Researchers worldwide are paying increasing attention on the health risks from exposure to IAPs in underground metro systems in cities such as Barcelona (Querol et al., 2012; Triadó-Margarit et al., 2017), Helsinki (Aarnio et al., 2005), Stockholm (Johansson and Johansson, 2002), London (Seaton et al., 2005), México city (Hernández-Castillo et al., 2014; Mugica-Álvarez et al., 2012), Los Angeles (Kam et al., 2011), Sao Paulo (Silva et al., 2012), Taipei (Cheng et al., 2012), Shanghai (Gong et al., 2017; Xu and Hao, 2017), Beijing (Li et al., 2006), Seoul (Hwang et al., 2010; Park and Ha, 2008), Manila (Hasselwander et al., 2022) and Sidney (Mohsen et al., 2018). In 2022, most literature studies focus on the exposure to PM_{10} and $PM_{2.5}$ (Jo et al., 2020; Johansson and Johansson, 2002; Loxham and Nieuwenhuijsen, 2019; Mohsen et al., 2018; Mugica-Álvarez et al., 2012; Querol et al., 2012), PM together with CO_2 (Gao et al., 2019; Hwang et al., 2017b; Park and Ha, 2008; Zheng et al., 2017) and bioaerosols (Coleman et al., 2018; Grydaki et al., 2021; Jo et al., 2020; Triadó-Margarit et al., 2017). Only few studies have focused on CO_2 alone, mainly employing theorical models to predict IAQ within underground metro systems (Wang et al., 2017). To understand IAQ in underground metro systems, it is important to understand the factors affecting IAPs exposure and their integrated relationships (Wang et al., 2017).

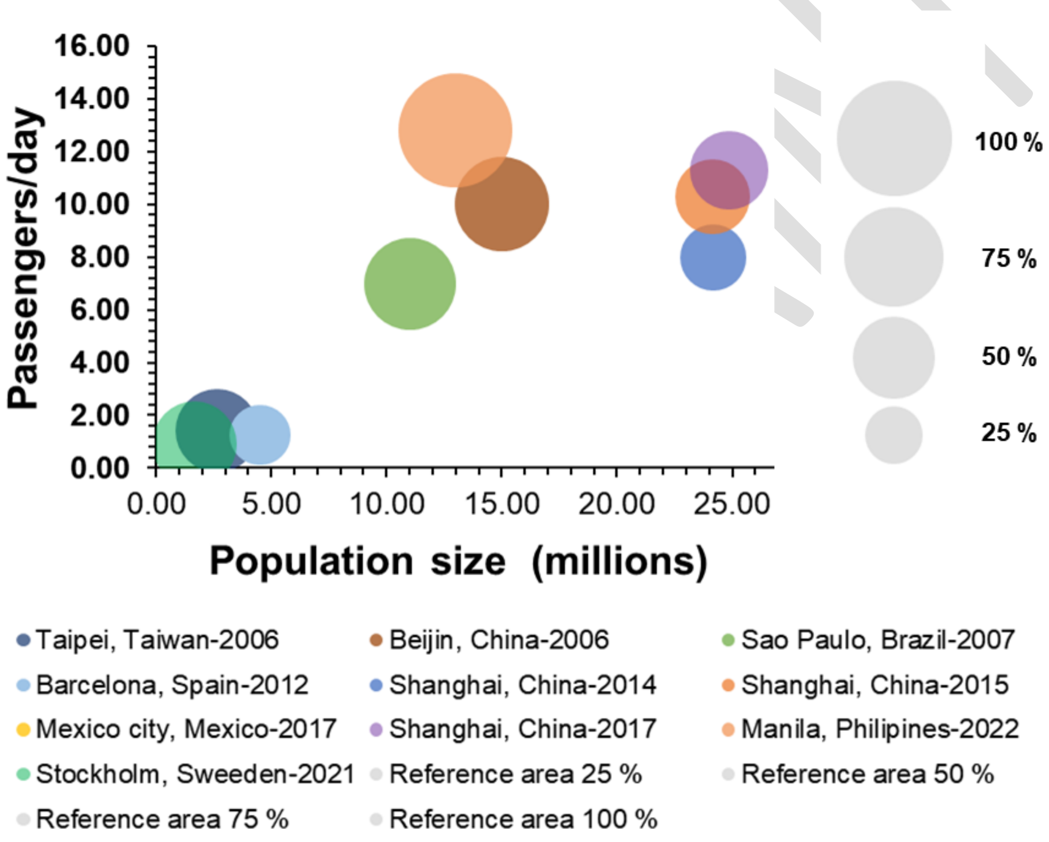


Fig. 5. Bubble diagram representing the passenger flow for cities with different population sizes. Bubble size represent the relative percentage of the population that uses the underground metro system compared to the total city population. The area of the symbols shows the ratio between the passenger's flow (x-axis) within the population size (y-axis). Gray symbols at the right part of the figure are placed to have a reference of the area sizes.

The principal factors affecting IAPs exposure levels in underground metro systems can be classified into two big categories: 1) carriage related factors like carriage ventilation quality, service time, train speed, train frequency, wheels and brake materials, commuting time and passenger net flow into the carriage

(Cepeda et al., 2017; Gong et al., 2017; Grydaki et al., 2021; Martins et al., 2016, 2015; Mugica-Álvarez et al., 2012; Passi et al., 2021; Shen and Gao, 2019; Wen et al., 2020; Xu and Hao, 2017) and 2) underground metro platforms factors related such as underground station ventilation, passenger net flow into the underground metro platform, platform screen doors, rails materials and outdoor environment characteristics (Gao et al., 2019; Kyritsi and Michael, 2020; Passi et al., 2021; Shen and Gao, 2019). Most of these factors are mutually related. For example, shorter commuting times have a dual effect on passenger net flow into platforms since some stations will have higher passenger frequency while others will remain less occupied for longer periods. Depending on the train speed and the dimensions of the tunnel, the air pushed by the front and the air sucked behind the train (piston wind effect), will generate more or less intense air currents near the platform (Moreno et al., 2014).

Ventilation is one of the most effective ways to optimize the complex physical environment in underground metro system, but it exerts a dual effect on IAQ (Wen et al., 2020). Figure 6 summarizes the main aspects to consider for ventilation in underground transport vehicles. On one hand, ventilation controls temperature, humidity and IAQ to ensure human comfort and health. On the other hand, ventilation carries potential risks of spreading air pollutants or carrying outdoor pollutants and produces continuous noise.

Thus, an efficient ventilation system should help to maintain IAQ and occupants comfort limiting the transport of air pollutants from the outdoor environment (Godish, 1996; Jaakkola and Miettinen, 1995). According to the ASHRAE standard 62-1989 on “Ventilation for Acceptable IAQ”, a fresh air supply of 8 L/s (28.8 m^3/h) per person is recommended for vehicles, waiting rooms, and platforms in transport systems (Persily, 1993; Steele and Brown, 1989). Wang et al. (2017) divided underground metro stations ventilation into three operating modes: 1) open operation mode is limited to air exchanged between indoor environment and outdoor environment through fans, ducts, and other facilities; 2) close operation mode provides fresh air to passengers by air-conditioning systems plus some fresh air introduced from station entrances and exits under the action of piston wind; and 3) platform screen door system, where the station uses air-conditioning systems for cooling and the tunnel uses piston action ventilation or mechanical ventilation for air exchanges with the outside atmosphere. For ventilation inside the train, mechanical ventilation, i.e., air conditioning, is the most effective ventilation system to control IAQ by removing IAPs (Passi et al., 2021; Xu et al., 2016). Despite this, underground metro carriages showed 20-50% higher CO_2 concentrations than those in aboveground carriages in Taipei metro system (Cheng et al., 2012; Cheng and Yan, 2011). Cheng et al. (2012, 2011) concluded that exhalation of commuters combined with poor ventilation inside underground metro carriages led to CO_2 concentration values that exceed the limit of 1000 ppm$_v$ proposed by the Taiwan EPA in 8 h. Similar CO_2 concentrations were measured inside the underground metro carriages of Los Angeles (USA) underground metro system, where CO_2 level reached up to 1200 ppm$_v$ mainly due to CO_2 build up inside the train (Kam et al., 2011).

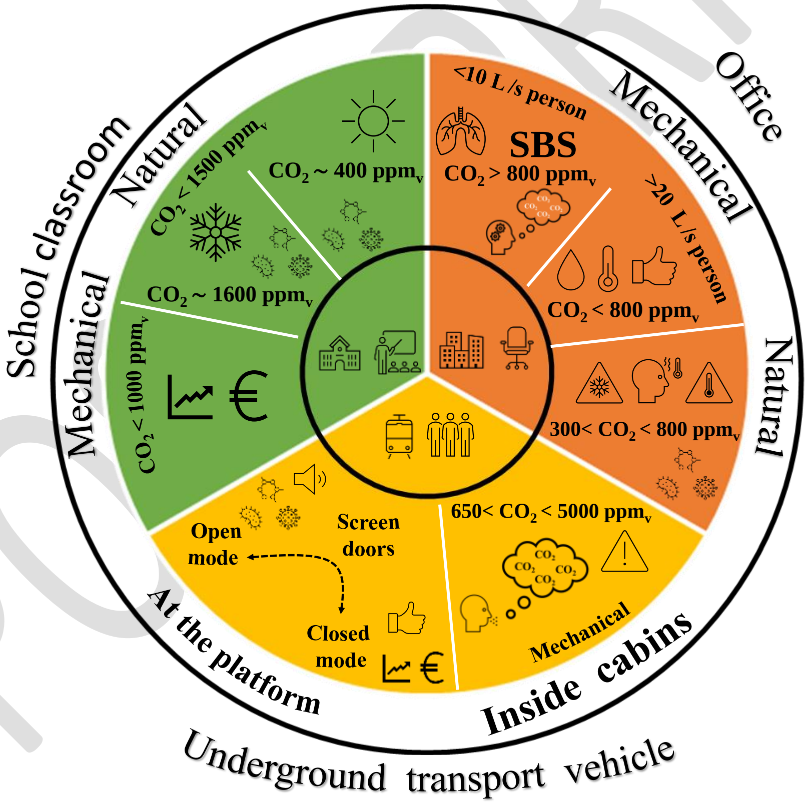


Fig. 6. Schematic diagram summarizing the ventilation requirements for all three different indoor environments considered in this study.

A research study performed a thorough monitoring campaign consisting of 3,528 samples of in-carriage CO_2 concentrations measured in 100 stations (44% of the 251 stations) of a city in northern China (Gao et al., 2019). From the four lines considered (orange, blue, red and yellow line), only one line (yellow line) was above ground, while the rest where underground lines. The effect of factors such as platform screen doors and passenger density were thoroughly investigated. Results showed that CO_2 concentration ranged between 650 and 5525 ppm_v, where lowest CO_2 concentration was observed in the stations equipped with enclosed platform screen doors (blue and orange line), followed by those with half-height platform screen doors (yellow), while those stations without platform screen doors exhibited the highest CO_2 concentrations inside metro carriages (red line) (Gao et al., 2019). Interestingly, the lines with the maximum passenger density during peak hours (8 to 8.4 p/m^2) exhibited the lowest CO_2 concentrations inside metro carriages, principally because they were equipped with platform screen doors. Platform screen doors reduce the air flow exchange between the platform with passengers waiting the train, and the indoor environment inside metro carriages. Another study measured CO_2 concentration in 100 underground Seoul Metro subway stations to determine which environmental factors and underground characteristics (station area, construction year, number of passengers, etc.) influenced the most IAQs in the stations (Hwang et al., 2017b). The average CO_2 concentration was 563.1 ± 77.2 ppm_v with a peak of 652.3 ± 55.6 ppm_v. CO_2 concentration exhibited a positive correlation with the number of passengers and the station area, while no correlation was found with construction year and station depth (Hwang et al., 2017b). High CO_2 concentrations were reported in another study performed in 108 stations (aboveground and underground) in Seoul, where CO_2 concentration was adopted as an indicator of the effectiveness of ventilation system (Park and Ha, 2008). The CO_2 concentration inside carriages ranged from 1,153 ppm_v to 3,377 ppm_v during peak time, with an average value of 1,775 ppm_v, exceeding the threshold value of 1,000 ppm_v due to the lack of fresh air supply into the interior of the trains. This highlights the strong correlation between CO_2 concentration and a great number of passengers (Li et al., 2006).

The large variability in CO_2 concentrations in metro systems worldwide suggest that the solutions for CO_2 removal may vary widely and may not rely solely on engineering solutions, but also service availability and the adjustment of peak hour behaviours in the population of interest. Well-designed ventilation systems in underground transport have proved to minimize and control indoor CO_2 concentrations. However, most works in the literature still report CO_2 concentrations up to 8.3 times higher than atmospheric CO_2 concentration (407.8 ±0.1 ppm). Therefore, underground metro carriages show a great potential for the installation of an iCO_2-DAC technology, since the concentrations commonly found in this type of indoor environment can help to overcome thermodynamical limitations of CO_2 direct air capture technologies.

4. Future perspectives

Through this work we demonstrated the urgent need to place more focus into indoor environments, where we spend most of our time, and the potential of iCO_2-DAC to generate a renewable carbon source to replace fossil fuels as a carbon feedstock in the chemical industry. Development of renewable carbon sources is the inevitable path that must be pursued to fight climatic change. Development of processes and solutions to capture and re-utilize atmospheric CO_2 will decrease the extraction of further carbon from the geosphere, slowing down the increase of atmospheric CO_2 concentration. Ideas and concepts must be placed in action, since as we move into a more sophisticated lifestyle, with increasing energy and materials needs, it urges to develop technologies not only capable of producing green energy and materials, but also capable of removing CO_2 from the atmosphere.

Despite ventilation and other control strategies, indoor air in school classrooms, office rooms and underground transport carriages reported CO_2 concentrations exceeding the IAGVs for their respective environment. Controlling the CO_2 concentration down to the IAGVs is a complex task to perform. In this sense, deploying CO_2 capture devices to improve IAQ in densely occupied buildings is a potential win-win opportunity. Carbon-neutral buildings can be developed, mitigating negative health effects and cognitive performance decrease of the occupants and minimizing the outdoor air supply and the energy consumption on air conditioning. CO_2 DAC technologies were originally conceived to capture CO_2 from extremely diluted (ca. 400 ppm_v) outdoor ambient air. Such technology could benefit of the better adsorption thermodynamic resulting from the higher CO_2 concentration in indoor air. Reports in the literature indicate that the technology is mature to introduce CO_2-DAC into human occupied buildings to carry out CO_2-DAC at atmospheric pressure, and under mild operation conditions (ambient temperature for adsorption and 80-100 °C for desorption).

One envisioned solution to produce valuable commodity chemicals based on CO_2 from indoor environments is presented in figure 7. The proposed process aims to capture CO_2 from indoor air environments and transform it into biofuels such as methane or alcohols that can be used on-site to provide heating. Producing such biofuels on-site will also reduce costs and emissions deriving from producing and transporting conventional combustibles. This technology should be envisioned as a complementary unit with similar operating and technical complexity to current Heating, Ventilation and Air Conditions (HVAC) units installed in multiple facilities. In the long run, the envisioned technology could even replace HVAC systems by a more sophisticated unit that is not only capable of providing heat, ventilation and air conditioning, but also to remove IAPs such as CO_2.

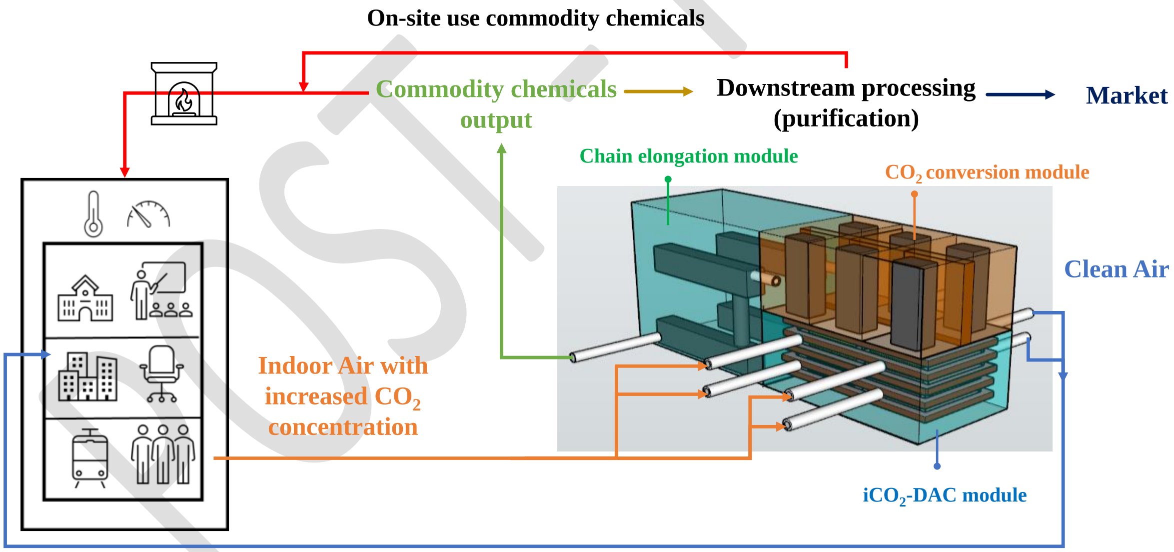


Fig. 7. Envisioned solution to produce valuable commodity chemicals based on CO_2 from indoor environments

The operating principle of the schematic process diagram presented in Figure 7 is detailed as follows. A CO_2 containing indoor air stream flows into the iCO_2-DAC module, where CO_2 is adsorbed and a stream of CO_2-free air is released back to the room. The CO_2 can be then desorbed from the CO_2 concentrator module, generating a high purity CO_2 stream that can act as a feedstock for the production of valuable chemical products. Among the CO_2 conversion technologies under development, those using electric energy as reducing power, *i.e.*, electrochemical and bioelectrochemical CO_2 reduction, are particularly suited for application in indoor environments, as the conversion modules can be easily connected to the already available electricity lines as stand-alone units. Electrochemical/bioelectrochemical units can be designed and operated to produce carbon-neutral methane, or even liquid fuels such as ethanol or butanol, which can be used on-site for heating the buildings, or as transportation fuel (Grim et al., 2020). Nearly pure (98.1%) methane production has been reported in bioelectrochemical cells at rates above 200 $L/m^2/d$, with electricity-to-methane conversion efficiency above 80% (Zhou et al., 2021), making it suitable for direct combustion in boilers for heat generation. More valuable liquid fuels such as ethanol and butanol have been produced both electrochemically (Karapinar et al., 2021; Rui et al., 2020; Shang et al., 2021) and bioelectrochemically (Romans-Casas et al., 2021; Srikanth et al., 2018) , although at lower purity and concentrations, requiring downstream processing before utilization. The goal of the envisioned technology goal is not only to improve IAQ by capturing CO_2, but also to be part of the future of green buildings by integrating management of human experience by improving subjective and objective indoor environmental quality (IEQ), and to reach environmental objectives such as circularity of resources and energy. In this sense, there are many challenges that need to be addressed within the upcoming years to facilitate the integration of such envisioned technologies within indoor environments (schools, office buildings and transportation vehicles). For example, utility rooms are mostly present in large office or public buildings, while some indoor spaces, such as schools or transportation vehicles, have no utilities rooms, or very small ones, that will not allow for the installation of additional instrumentation and processes. Thus, new indoor environments should be designed including the space for indoor pollutants treatment, recycling, and conversion. Furthermore, several technical challenges need to be resolved to miniaturize and optimize the capture and conversion units to avoid the occupancy of large spaces for producing and storing biofuels from CO_2.

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