The atmospheric signature of carbon capture and storage

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Compared with other industrial processes, carbon capture and storage (CCS) will have an unusual impact on atmospheric composition by reducing the CO2 released from fossil-fuel combustion plants, but not reducing the associated O2 loss. CO2 that leaks into the air from below-ground CCS sites will also be unusual in lacking the O2 deficit normally associated with typical land CO2 sources, such as from combustion or ecosystem exchanges. CCS may also produce distinct isotopic changes in atmospheric CO2. Using simple models and calculations, we estimate the impact of CCS or leakage on regional atmospheric composition. We also estimate the possible impact on global atmospheric composition, assuming that the technology is widely adopted. Because of its unique signature, CCS may be especially amenable to monitoring, both regionally and globally, using atmospheric observing systems. Measurements of the O2/N2 ratio and the CO2 concentration in the proximity of a CCS site may allow detection of point leaks of the order of 1000 ton CO2 yr\(^{-1}\) from a CCS reservoir up to 1 km from the source. Measurements of O2/N2 and CO2 in background air from a global network may allow quantification of global and hemispheric capture rates from CCS to the order of \(\pm 0.4 \text{PgC yr}^{-1}\).

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1. Introduction

From a geochemical perspective, the processes contributing to increases in atmospheric CO2 can be grouped into discrete categories, each with distinct geochemical fingerprints. Fossil-fuel burning, for example, releases CO2 and consumes O2 in characteristic ratios depending on the fuel type, leading to small but detectable deficits in the atmospheric O2/N2 ratio in proportion to

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the CO₂ excess. Fossil-fuel burning also enriches the $^{12}$C content of atmospheric CO₂ relative to the $^{13}$C and $^{14}$C contents of CO₂, leading to declines in the $^{13}$C/$^{12}$C and $^{14}$C/$^{12}$C ratios [1]. Similarly, sources or sinks of CO₂ from the land biosphere lead to changes in atmospheric CO₂ that are strongly anticorrelated to changes in the atmospheric O₂/N₂ ratio and in the $^{13}$C/$^{12}$C ratio of CO₂, while sources or sinks of CO₂ from the ocean, mostly involving inorganic chemical reaction in sea water, have little impact on the atmospheric O₂/N₂ ratio or the $^{13}$C/$^{12}$C ratio of CO₂. Programmes to measure changes in atmospheric O₂/N₂, $^{13}$C/$^{12}$C or $^{14}$C/$^{12}$C have exploited these differing fingerprints to separate CO₂ sources and sinks into contributions from different geochemical processes such as land or ocean uptake, or fossil-fuel burning (e.g. [2–5]).

Carbon capture and storage (CCS), a technology that may allow continued use of fossil fuels as an energy source while avoiding the associated CO₂ emissions [6–8], will also have distinct geochemical fingerprints. CCS involves capturing the CO₂ that would otherwise be emitted from large stationary CO₂ sources, such as power plants, and storing it in permanent or quasi-permanent geologic reservoirs, such as saline aquifers, depleted oil reservoirs or below the sea floor. A related idea is to capture CO₂ directly from the atmosphere, an approach known as direct air capture (DAC) [9–11]. CCS and DAC represent novel geochemical processes, largely without parallel on Earth today.

The effect of CCS on atmospheric composition will be more complex than simply the avoided CO₂ concentration increases. While reducing CO₂ emissions from combustion, CCS will not reverse the atmospheric O₂ loss and the associated impact on the atmospheric O₂/N₂ ratio. The exhaust plume of a power plant equipped with CCS will thus contain an O₂ deficit comparable to an unmodified power plant, but without the accompanying normal excess of CO₂. CCS will thereby reduce the spatial gradients and short-term variability in CO₂ while leaving the spatial gradients and short-term variability in O₂/N₂ ratio unchanged, compared with a world without CCS. CCS will also reduce the gradients and variability in the isotopic composition of CO₂. These reductions will occur both in the near-field of a power plant, as well as at much larger continental, hemispheric and global scales.

Globally, the net effect of CCS will be to reduce CO₂ buildup without any effect on O₂ loss. As a storage mechanism for CO₂, therefore, CCS will resemble oceanic CO₂ uptake, which similarly reduces CO₂ buildup without impact on O₂ [12]. However, CCS will leave a strong signature on the isotopes of CO₂ by lessening the strong isotopic imprint of fossil-fuel burning. By contrast, oceanic CO₂ uptake has weaker isotopic influences.

CO₂ pumped below ground will typically form a buoyant supercritical fluid, tending to migrate upwards unless contained below a continuous caprock [6]. Even where the caprock appears continuous, leakage could occur through the injection well if not properly sealed, leading to a point source at the well, or via permeation through the caprock, leading to widespread areal leakage. Leakage could also occur through old abandoned wells that are not properly sealed or through faults in the caprock, leading to a source spread along a line at the surface or at hot-spots [13]. Leaked CO₂ will have characteristic atmospheric fingerprints, typically resembling fossil-fuel CO₂ in its isotopic composition, but not accompanied by the normal atmospheric O₂ deficit expected from a fossil-fuel CO₂ source [14].

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Developing methods to detect leakage from geological CO2 sequestration sites is critical to ensure that the objectives of the sequestration process are being met and to avoid safety concerns. Haefeli et al. [15] note that proper accounting of both capture efficiency and leakage is required under the United Nations Framework Convention on Climate Change, and leakage may need to be kept near or below 0.01 per cent per year to meet targets for stabilization of atmospheric CO2 concentrations in all cases. For a large-scale storage site containing 10 Mton CO2, this corresponds to a leakage rate of 1000 ton CO2 yr\(^{-1}\) or 32 g CO2 s\(^{-1}\) [16]. Seismic or electromagnetic methods may prove useful for tracking CO2 flow below ground, and soil sampling may help detect CO2 plumes near the surface, but these may not be sufficient to quantify leakage accurately or to rule out leakage through faults or wells. Soils naturally contain excess CO2 from plant and microbial respiration, which may mask any excess from leakage. Chemical tracers, such as SF6 or perfluorocarbons, may be injected along with the CO2 to aid in leak detection [17]. Tracer injection has additional up-front and detection costs, however. Also, the migration of the tracer below ground may not exactly track the migration of CO2, and its presence may raise other environmental concerns [16]. If full advantage is taken of the unique geochemical fingerprints of CO2 leaking from geological sequestration, however, tracer injection might not be necessary.

The introduction of CCS will present both new challenges and new opportunities for atmospheric measurement programmes. Existing approaches to calculating natural land and ocean carbon sinks using measurements of O2 concentration or carbon isotopes involve accounting for direct human impacts (e.g. from fossil-fuel burning and land use) on atmospheric composition from bottom-up accounting methods. The natural sinks are then calculated from the residual changes in atmospheric composition not accounted for by the direct human impact [3,18]. The extension of these methods into an era with CCS will require that rates of CCS and leakage from CCS sites also be well quantified. How well this will work in practice remains unclear. Bottom-up reporting may become less, not more, reliable once CO2 has a ‘price tag’, with built-in financial incentives to under-report CO2 sources, such as fossil-fuel burning, and to over-report sinks, such as CCS [19]. On the other hand, with steady improvements in our ability to understand and quantify land and ocean processes, it may be possible to turn the calculations around, calculating the financially relevant direct human components, such as fossil-fuel burning, land use, or CCS, from the change in atmospheric composition not accounted for by the (independently known) land and ocean sinks. CCS may be especially amenable to such an approach given its unique atmospheric signatures.

In this paper, we consider in detail two aspects of CCS’s atmospheric signature. First, we illustrate the potential use of atmospheric measurements for both assessing capture efficiency and detecting leakage from below-ground sequestration sites. Second, we use simulations to illustrate the complex implications of CCS on global trends in CO2, O2/N2 and CO2 isotopes. Even though wide adoption of CCS to mitigate CO2 emissions is at least a few decades away, both of these subjects already have relevance—the first because leak detection is a major issue already for pilot CCS projects, and the second because the possible growth of CCS is already relevant for the global observing systems planned to extend over decades.
To explore atmospheric signatures near a CCS site, we turn to the atmospheric modelling study of Leuning et al. [16] who simulate changes in atmospheric composition from a hypothetical leak at the Otway Basin Pilot Project in southeastern Australia. The simulations, using a three-dimensional transport model [20], assume a leak rate of 1000 ton CO₂ yr⁻¹ and also allow for a secondary source from a processing plant of 8800 ton CO₂ yr⁻¹. The simulations reproduced here assume that the leakage involves a point source. Atmospheric variations are examined at a ‘detection site’ 700 m northeast of the leak. The processing plant is assumed to be 2000 m due north of the source. Although the Otway Basin Project will inject CO₂ of magmatic origin (δ¹³C ≈ −6‰) extracted from natural gas, we assume here, for illustrative purposes, that the CO₂ is derived from a coal-fired power plant equipped with CCS with a capture efficiency of 90 per cent, a more typical target for scaled-up future applications.

By convention, ¹³C/¹²C variations are expressed as deviations from a standard in delta notation, \( \delta^{13}C = \left( \frac{R}{R_{\text{std}}} - 1 \right) \), where \( R \) and \( R_{\text{std}} \) are the ¹³C/¹²C ratio of the sample and standard, respectively, and \( \delta^{13}C \) is multiplied by 1000 and expressed in parts per thousand (%). O₂/N₂ ratios are also expressed in delta notation, \( \delta(O_2/N_2) \), except that the relative deviation from the O₂/N₂ standard is multiplied by 10⁶ and expressed as ‘per meg’. For coal, \( \delta^{13}C = -26‰ \) is assumed, with 1.15 mol of O₂ consumed per mole of C produced [21], leading to 11.5 mol of O₂ consumed for every mole of CO₂ that escapes the capture process, considering that 90 per cent of the CO₂ is captured. The capture process is assumed to be associated with a −5‰ fractionation in ¹³C/¹²C, roughly consistent with fractionation associated with CO₂ capture by lime, which is dominated by kinetic effects [22]. With this assumption, mass balance requires that the captured CO₂ has an isotopic composition of −26.5‰ and CO₂ released from the processing plant has an isotopic composition of −21.5‰. The isotopic composition of the captured CO₂ is very similar to the original coal, owing to the high efficiency of the capture process. The background atmosphere is assumed to have a CO₂ concentration of 374 ppm, \( \delta^{13}C \) of −8.1‰ and \( \delta(O_2/N_2) \) of −350 per meg.

Simulated changes at the detection site over a 6-day period are shown in figure 1 under generally southwesterly wind conditions. The CO₂ simulations are as published by Leuning et al. [16]; here, we also show changes in \( \delta^{13}C \) and O₂/N₂ computed directly from the changes in CO₂, taking into account the characteristic O₂ : C and \( \delta^{13}C \) signatures of the sources given above. Discrete CO₂ peaks are seen in the simulations corresponding to troughs in \( \delta^{13}C \) and O₂/N₂. These peaks occur when the exhaust plumes from the leak or the processing plant pass directly over the detection site. There is minimal intermixing of the two plumes, so that individual peaks are directly attributable to one source or the other. The peaks from the processing plant are in the 5–10 ppm range, whereas those from the leak are in the 1–3 ppm range. The processing plant peaks are accompanied by declines (300–600 per meg) in the O₂/N₂ ratio, whereas those from the leak produce no changes in the O₂/N₂ ratio. The magnitude of the peaks and their characteristics are highly dependent on the wind regime for the 6-day period. Under light winds or highly stratified conditions (e.g. at night), much larger changes would be expected, with the plumes intermixing to some degree.

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The model depicts only part of the full variability to be expected at the detection site, as it neglects variations driven by local vegetation or other local sources and variation in the background atmosphere. CO$_2$ exchange with vegetation and soils typically drives a diurnal cycle in CO$_2$ concentrations near the ground, driven by the day–night cycle of net photosynthesis/respiration and the day–night cycle in vertical mixing [23]. In a stable nocturnal boundary layer, CO$_2$ concentrations can rise above the free-tropospheric background by tens to hundreds of parts per million, while day-time values typically drop below free tropospheric values only by a few parts per million. Field studies show that the near-surface CO$_2$ variations are typically strongly correlated with variations in the $^{13}$C/$^{12}$C ratio of CO$_2$ and the O$_2$/N$_2$ ratio [23–26]. The correlations depend, in the case of $^{13}$C/$^{12}$C, on the average isotopic composition of the CO$_2$ that is added or removed by vegetation, and in the case of O$_2$/N$_2$ on the oxidative state of the organic matter that is being created or destroyed as well as the cycling of nitrogen [27].

In figure 2, we superimpose the model simulations of the Otway Basin on a scatter plot from observed variations in CO$_2$ and $^{13}$C/$^{12}$C of CO$_2$ from a coniferous forest in Colorado, USA [24]. This superposition illustrates certain features to be expected downwind of a generic sequestration site where natural...
variability is also present. The Colorado data fall roughly along a straight line with a slope corresponding to the addition of CO₂ with δ¹³C ≈ −26‰ and with day-time values on the upper right (lower CO₂) of the plot and night-time values distributed over the remainder of the plot. The scatter of the data about the line is dictated mostly by instrumental precision in the isotopic measurement. The covariations in CO₂ and δ¹³C from the CCS leak lie along a straight line that has virtually the same slope as the ecosystem-driven exchanges, as expected since both sources have nearly the same isotopic signature of −26‰. For detecting leakage, it can be seen that the δ¹³C data would provide little information not already contained in the CO₂ data.

For the δ¹³C data to be useful for leak detection, the exogenous CO₂ from CCS must have a distinctly different isotopic composition from CO₂ of other nearby sources. However, the isotopic composition of most coals and petroleum lies in the range of −24 to −30‰ [28], similar to the range for most ecosystems [29]. δ¹³C data may nevertheless have value in some specific situations, such as detecting emission of thermogenic CO₂, which often must be removed as a contaminant from natural gas, and may have δ¹³C as high as −6‰. Based on the scatter in figure 2, it would appear that a thermogenic plume of the order of 4–5 ppm would be readily distinguishable from the natural variability. CO₂ from natural-gas combustion, which can be as low as −45‰, would be readily detectable. Isotopic measurements would also be more helpful if the local ecosystem were dominated by C₄ grasses (δ¹³C ≈ −13‰), and may have value for distinguishing residual CO₂ emissions from CCS processing plants (as shown in figure 2), since the residual CO₂ will be offset by the fractionation associated with the capture process.
Figure 3 shows a similar superposition of the Otway Basin simulation on a scatter plot of $O_2/N_2$ versus $CO_2$ from a site in central Siberia [26]. Again, we consider this juxtaposition of synthetic and real data to illustrate the main features to be expected downwind of a generic sequestration site, allowing also for variability from local vegetation and the background atmosphere. The Siberian data tend to fall along a straight line with a slope of around $-5.03$ per meg ppm$^{-1}$, corresponding to a molar $O_2/CO_2$ exchange ratio of $-1.05$, with daytime data in the upper left and night-time data spread across the rest of the plot. Similar measurements for a forest site in Wisconsin also show very strong covariations with similar slopes ($O_2/C$ approx. 1.01–1.10) [25]. Urban areas may have different ratios reflecting fossil-fuel combustion, but even in urban settings, tight correlations are observed [30]. The plumes from the leak and the processing plant have characteristic slopes on the $O_2 : CO_2$ plot that are different from each other as well as different from that of the ecosystem. Based on the scatter of the data about a linear relationship, a leakage detection limit of around 2–4 ppm $CO_2$ is implied by the Siberian and Wisconsin data.

The processing plant plume would be especially easy to detect because it involves readily detectable declines in $O_2/N_2$ ratio that deviate markedly from the natural relationship. This plume lies along a line on the plot with a slope,
when expressed in molar \( (O_2 : C) \) units, equal to \( r_f / (1 - e) \), where \( r_f \) is the O₂ : C combustion ratio of the coal and \( e \) is the processing plant capture efficiency \((0 < e < 1)\). The combustion ratio \( r_f \) of coals can be directly determined from their elemental composition. Combining elemental composition data with atmospheric measurements thus provides a means to measure \( e \) remotely. This approach may prove more accurate than assessments based on stack emissions [31]. One complication, however, is that releases of O₂-deficient (i.e. N₂-rich) waste air and CO₂ from capture plants may not always be perfectly collocated in space and time, leading to several distinct plumes from the plant itself, one depleted in O₂ and the other enriched in CO₂.

The leakage plumes as simulated for Otway Basin (solid line in figure 3) would be somewhat difficult to detect against the variability seen in the Siberian data. This scatter is mostly due to instrument imprecision, which could be improved by a factor of three or more. Ultimate sensitivities to CO₂ leakage of the order of 1–2 ppm seem feasible, which would be sufficient for detecting point source leaks of the order of 1000 ton CO₂ yr⁻¹ at distances of the order of 1 km under modest wind conditions, as depicted for the Otway Basin simulation [16].

Obtaining high-precision field measurements will be essential for definitive leak detection. Bowling et al. [24] report a precision for 6 min average \( \delta^{13}C \) determinations using a tunable diode laser system of \( \pm 0.15\%_e \) or better. For O₂/N₂, an expanding range of high-precision techniques has been developed in recent years. Kozlova & Manning [32] report a precision of \( \pm 1.5 \) per meg for approximately 20 min determinations using a paramagnetic technique. Stephens et al. [25] report precisions for 1 min average O₂/N₂ ratio of \( \pm 2.5 \) per meg based on a modified commercial fuel-cell analyser, while Stephens et al. [33] report a precision of \( \pm 1.1 \) per meg for a 5 min average using a technique based on light absorption at 147 nm. Fessenden et al. [14] report promising results from a pilot study to detect leakage of CO₂ using combined O₂/N₂ and CO₂ measurements. These techniques would appear to be ripe for considerable further refinements and cost reductions, particularly if economies of scale come into play. With suitable characterization of local variability, it appears possible to detect signals of a few parts per million CO₂ from leakage under general conditions.

3. The global signature of carbon capture and storage

We now turn to the question of how global atmospheric trends of CO₂ concentration, O₂/N₂ ratio and the carbon isotopes of CO₂ would be impacted by wide adoption of CCS in the future. Our approach involves comparing a baseline scenario, which assumes no mitigation efforts, with alternative scenarios that incorporate mitigation. For the baseline, we adopt the B1-IMAGE scenario from the Intergovernmental Panel on Climate Change Special report on emissions scenarios [34]. The B1-IMAGE scenario assumes a future world in which energy and land usage are guided by a high level of environmental consciousness, but in which no specific measures are taken to mitigate climate change. B1-IMAGE is an appropriate baseline scenario because mitigation efforts such as CCS are not likely to be implemented on a wide scale unless other measures are also taken to reduce emissions, such as energy conservation.
We also consider four alternative ‘mitigation’ scenarios in which CO₂ emissions are reduced (compared with B1-IMAGE) by an amount that grows linearly from 0 to 2 Pg C yr⁻¹ over the 50-year period from 2010 to 2060 and remains constant (at 2 Pg C yr⁻¹) thereafter. In other words, the mitigation scenarios effectively assume two ‘wedges’ of mitigation, according to Pacala & Socolow [35]. (A ‘wedge’ refers to a 1 Pg yr⁻¹ reduction in emissions in over 50 years [35].) The four mitigation scenarios differ from each other in how the emission reductions are achieved: (1) CCS, (2) energy conservation, i.e. averted fossil-fuel usage, (3) land carbon sequestration, or (4) DAC of CO₂. Land carbon sequestration is assumed to occur via reforestation or afforestation, etc. Although our emphasis here is primarily on the atmospheric imprint of CCS (scenario 1), the other scenarios are useful for comparison purposes.

To predict the future changes in CO₂ and related tracers, we use a simple coupled reservoir model, in which the ocean is described by a ‘box diffusion’ type of model [36,37], and the land biosphere and atmosphere are each described as single well-mixed reservoirs. The model accounts for ocean uptake of CO₂ due to inorganic carbon chemistry and ocean mixing, and it accounts for CO₂ uptake by the land biota by assuming that net primary production increases linearly with CO₂ concentration. This model provides a means to account for the effects of human emissions (fossil-fuel burning, land-use change, mitigation measures), for land and ocean carbon sink processes, and for so-called isofluxes between the atmosphere and the land biosphere and oceans, which involve swapping of atoms between reservoirs, without any net gain or loss in any reservoir. Isofluxes influence the ¹³C/¹²C and ¹⁴C/¹²C ratios of CO₂ without changing atmospheric CO₂ abundance.

Simulations are carried out allowing for variations in emissions according to the B1-IMAGE scenario starting in year 2005, with emissions prior to 2005 based on records compiled by the Carbon Dioxide Information and Analysis Center [38,39]. The simulations for CO₂, for the ¹³C/¹²C ratio of CO₂ and for atmospheric O₂/N₂ ratio involve ‘forward’ model runs, in which concentrations (or ratios) are computed for specified human emissions. For the ¹⁴C/¹²C ratio, the model is run up to year 2005, with the atmospheric ¹⁴C/¹²C ratio specified to match observations, thus implicitly accounting for the input of ‘bomb’ ¹⁴C from the atmospheric nuclear weapons tests in the mid-twentieth century. After 2005, the simulated ¹⁴C/¹²C ratio is carried out in ‘forward’ mode, assuming no additional anthropogenic ¹⁴C source. The parameters governing ocean and land carbon uptake and isotopic exchanges are tuned to match the observed changes over the twentieth century in CO₂ concentration, to match the ocean radiocarbon inventory and to match the observed atmospheric ¹⁴C/¹²C trend since year 2000 without any bomb input. The model uncertainties have little impact on our analysis, which focuses on the differences between the scenarios, rather than the absolute predicted changes.

The simulations account for temporal changes in the composition of global average fossil fuel based on the changing emissions of discrete fuel classes from the B1-IMAGE scenario [34] and emission factors (for ¹³C/¹²C and O₂ : C) of different fuel classes [21,28]. For the CCS and energy conservation scenarios, the reduced emissions are assumed to involve fossil fuel with global average composition. Land sequestration is assumed to involve photosynthesis with a molar O₂ : C ratio of 1.1 and an isotopic fractionation in ¹³C/¹²C of −18‰. The CO₂ source from land-use
change is assumed to have a $^{13}\text{C}/^{12}\text{C}$ ratio identical to the contemporaneous land biosphere and with an $O_2/C$ ratio of 1.1. CCS and DAC are assumed to occur with $0\%$ and $-5\%$ fractionation in $^{13}\text{C}/^{12}\text{C}$, respectively. The $^{14}\text{C}/^{12}\text{C}$ changes are simulated following the formalism of Siegenthaler & Oeschger [40], leading to results in standard delta notation ($\Delta^{14}\text{C}$), where, for example, $\Delta^{14}\text{C} = 100\%$ corresponds to a $^{14}\text{C}/^{12}\text{C}$ ratio 10 per cent larger than the isotopic standard, after correcting for the offset in the $^{13}\text{C}/^{12}\text{C}$ ratio. Model results for $^{13}\text{C}/^{12}\text{C}$ are similarly reported in standard delta notation.

The projected net anthropogenic emissions and the associated rise in $\text{CO}_2$ are shown in figure 4, for both the baseline and mitigation scenarios. All four mitigation scenarios yield identical changes in $\text{CO}_2$ concentration, reflecting the identical net anthropogenic $\text{CO}_2$ emissions. In the baseline scenario, fossil-fuel and land-use emissions rise to a peak of approximately 12 Pg C yr$^{-1}$ around year 2040, falling thereafter (figure 4). $\text{CO}_2$ rises at a roughly linear rate until mid-century, slowing thereafter, and virtually stabilizing at approximately 500 ppm by year 2100. In the mitigation scenarios, the rise in $\text{CO}_2$ is similar until mid-century, but is slower thereafter, peaking in year 2084, with a very slight fall thereafter. Despite having identical trajectories in $\text{CO}_2$ concentration, the mitigation scenarios have different trajectories in $O_2/N_2$ ratio and carbon isotopes, which we discuss in turn.

Figure 4. (a) Projected changes in atmospheric $\text{CO}_2$ from the IPCC B1-IMAGE scenario (baseline scenario) and from a mitigation scenario in which emissions are reduced (see text). (b) Anthropogenic $\text{CO}_2$ emissions assumed for the scenarios. Simulations are based on a simple reservoir model (see text).
Figure 5. Projected future changes in atmospheric O$_2$/N$_2$ ratio versus CO$_2$ concentration for the baseline scenario and mitigation scenario depicted in figure 4. The mitigation scenario is shown with four alternatives, depending on the type of mitigation, with different consequences for O$_2$/N$_2$. Also shown are vectors indicating the influence of processes in isolation: land uptake (LND), fossil-fuel burning (FOS), ocean CO$_2$ uptake (OCE), carbon capture and storage (CCS), and direct air capture (DAC).

(a) O$_2$/N$_2$ ratio

Figure 5 shows the simulated changes in atmospheric O$_2$/N$_2$ ratio relative to CO$_2$ for the different scenarios. The inset arrows show the vector contributions from the various processes. The simulated trajectories are seen to have a steeper slope on the O$_2$/N$_2$ versus CO$_2$ plot than expected from fossil-fuel burning alone (FOS vector). The main reason, regardless of scenario, is that the CO$_2$ rise is reduced by oceanic uptake of CO$_2$, which has no effect on the decline in O$_2$/N$_2$ ratio. The slope is also slightly influenced for all scenarios by land-use emissions and by the modelled land sink, which combine to yield a small net land CO$_2$ sink and O$_2$ source. This sink has a lower O$_2$:C ratio than fossil-fuel burning, steepening the slope of the overall atmospheric trajectory. These same effects influence past trends [4]. The simulated atmospheric trajectory is also impacted by CCS and DAC, which act similarly to the ocean sink, offsetting the CO$_2$ rise but not the O$_2$ decline.

The fraction of CO$_2$ emissions absorbed by the oceans increases as the CO$_2$ growth rate slows, allowing the oceanic CO$_2$ excess to be mixed into a larger volume of the ocean. As a result, during the latter half of the twenty-first century, when CO$_2$ growth rate is much lower, the ocean plays a larger relative role in slowing the CO$_2$ rise. Because this behaviour of the ocean sink has no effect on O$_2$, the O$_2$/N$_2$ ratio declines increasingly faster for all scenarios compared with the CO$_2$ rise, with the changes most apparent late in the century. The O$_2$/N$_2$ decline continues even after CO$_2$ has peaked.

In the CCS and DAC mitigation scenarios, the change in O$_2$/N$_2$ ratio is even greater than in the baseline scenario without mitigation. This behaviour results because the production of O$_2$ by the natural land CO$_2$ sink is reduced in scenarios...
with lower CO$_2$. In the scenario with land carbon sequestration, the change in O$_2$/N$_2$ ratio is smaller than in the baseline scenario because of photosynthetic O$_2$ production. The energy conservation scenario has an even smaller drop in O$_2$/N$_2$ because of the higher O$_2$ : C ratio of fossil-fuel burning as compared with land photosynthesis.

(b) Atmospheric $^{14}$C

Figure 6 shows simulated changes in atmospheric $\Delta^{14}$C relative to changes in CO$_2$ concentration along with a vector inset showing the influence of the dominant processes. Most vector slopes can only be roughly indicated, because they are not strictly constant in time, but vary with absolute CO$_2$ concentrations and $\Delta^{14}$C value. Fossil-fuel burning adds CO$_2$ that is devoid of $^{14}$C to the atmosphere, thus driving the $^{14}$C/$^{12}$C ratio downwards, a process known as the Suess effect [41]. All scenarios yield trajectories on the plot with a slope smaller than expected from fossil-fuel burning alone.

Land and ocean CO$_2$ uptake have no effect on $\Delta^{14}$C because the isotopic fractionation associated with these processes is corrected for when expressing the $^{14}$C/$^{12}$C ratio in $\Delta$ notation. Land and ocean uptake thus tend to steepen the trajectories in figure 6 compared with the fossil-fuel burning vector. This effect is more than offset, however, by the isofluxes of $^{14}$C with the land and oceans, which buffer the decline via exchanges of C atoms between the atmosphere and the land and oceans. The $\Delta^{14}$C isoflux effect includes a diminishing contribution from the redistribution of bomb $^{14}$C excess. The main contribution, however, is from the redistribution of $^{14}$C-deficient fossil-fuel carbon. For all scenarios, the isoflux term increases in relative importance with time, causing the upward curvature of all scenarios in figure 6. This behaviour results because the isoflux buffering is more efficient than the ocean buffering of CO$_2$ concentration, reflecting the different impulse response functions of atmospheric CO$_2$ and carbon isotopes (e.g. [42]).
In all scenarios, the main factor driving the $\Delta^{14}C$ changes is the amount of fossil-fuel $CO_2$ released to the atmosphere. In figure 6, the CCS and energy conservation scenarios are indistinguishable, with $\Delta^{14}C$ declining less than the baseline scenario owing to the avoided emission of $^{14}C$-devoid fossil carbon. The land sequestration and DAC scenarios are also indistinguishable from one another. While both are displaced in figure 6 from the baseline scenario, the displacement is mostly due to differences in the $CO_2$ trajectory rather than the $\Delta^{14}C$ trajectory. Examined closely, however, the changes in $\Delta^{14}C$ for the land sequestration and DAC scenarios are also very slightly displaced (downwards) compared with the baseline scenario. The displacement is a dilution effect: while the same amount of $^{14}C$-devoid carbon is released by fossil-fuel burning, the impact on $\Delta^{14}C$ is greater if there is less $CO_2$ in the atmosphere. A similar dilution effect impacts every mitigation scenario relative to the baseline scenario.

Figure 7 shows the simulated changes in $\delta^{13}C$ relative to the changes in $CO_2$ concentration along with a vector inset showing the influence of the dominant processes. In most respects, the impacts on $\delta^{13}C$ are similar to those on $\Delta^{14}C$. As for $\Delta^{14}C$, the vector slopes for $\delta^{13}C$ can only be roughly indicated, owing to their sensitivity to the concentration and $\delta^{13}C$ level of atmospheric $CO_2$. Fossil-fuel $CO_2$ has a lower $\delta^{13}C$ level than atmospheric $CO_2$. Fossil-fuel burning (FOS vector) thus drives the atmospheric $\delta^{13}C$ level downwards. The downward trajectory in $\delta^{13}C$ in all scenarios is smaller, however, than expected from fossil-fuel burning alone mainly because of the impact of isofluxes. The isofluxes grow in relative importance with time, just as for $^{14}C$, leading to upward curvature in the plots.

The trajectories for $\delta^{13}C$ are qualitatively different from those of $\Delta^{14}C$ mainly because $\delta^{13}C$ is additionally sensitive to isotopic fractionation associated with the land, ocean and DAC sinks. The ocean $CO_2$ sink is associated with only weak fractionation, leading to a vector slope that is only slightly different from
zero (OCE vector). The land sink (LND vector), however, involves strong isotopic fractionation associated with photosynthesis. For the land sequestration scenario, this fractionation offsets the effect of fossil-fuel addition on both CO$_2$ and $\delta^{13}$C, leading to smaller changes in $\delta^{13}$C overall. All four mitigation scenarios involve sequestering or reducing emissions of $^{13}$C-depleted carbon. The CCS and energy conservation scenarios, in fact, have identical trajectories in figure 7. The land sequestration scenario differs very slightly from these, but the difference is not significant compared with uncertainties in model parameters, which govern this difference (future photosynthetic fractionation and the $\delta^{13}$C of fossil fuels). The DAC scenario has a $\delta^{13}$C trajectory similar to the baseline scenario, the main difference being the change in CO$_2$. The small $\delta^{13}$C change from the baseline scenario reflects two competing effects: the assumed $-5^{\circ}$‰ fractionation associated with DAC that drives $\delta^{13}$C higher, and a dilution effect equivalent to that mentioned above for $\Delta^{14}$C that drives $\delta^{13}$C lower.

4. Global verification of carbon capture and storage

The simulations suggest the possibility of detecting and quantifying rates of carbon capture at the global scale through combined tracer measurements. The CCS scenario stands out as being characterized by maximal changes in O$_2$/N$_2$ and minimal changes in $\delta^{13}$C and $\Delta^{14}$C compared with the other scenarios. The DAC scenario, in contrast, stands out by having maximal changes in all three tracers.

To assess the ability to quantify global capture rates, it is useful to consider the composite tracer ‘atmospheric potential oxygen’ (APO) [17,43] defined according to

$$\delta APO = \delta(O_2/N_2) + \left( \frac{1.1}{0.2095} \right) (X_{CO_2} - 350),$$

where 1.1 is an estimate of the relevant global average O$_2$:C ratio for land photosynthesis and respiration, 0.2095 converts from mole fraction to per meg units, $X_{CO_2}$ is the CO$_2$ mole fraction in parts per million, 350 is an arbitrary reference value of the CO$_2$ mole fraction and $\delta APO$ is expressed in per meg units. $\delta APO$ is largely conserved by land photosynthesis and respiration, which produce compensating changes in O$_2$ and CO$_2$. A process that captures 1 Pg C of CO$_2$ from the global atmosphere without impacting O$_2$ will decrease the global average CO$_2$ concentration and $\delta APO$ by 0.47 ppm and 2.47 per meg, respectively.

The main contributions to changes in $\delta APO$ are fossil-fuel burning, and air–sea exchanges of O$_2$, N$_2$ and CO$_2$, and possibly also carbon capture. Fossil-fuel burning reduces $\delta APO$ because it is characterized by an O$_2$:C ratio higher than 1.1. Subtracting fossil-fuel and air–sea gas exchange contributions from the observed total trend in $\delta APO$ will yield the contribution from CCS and DAC. Table 1 summarizes estimates of the impact on $\delta APO$ of various processes, along with estimates of their feasible observational accuracy. Our calculation suggests that it should be possible to estimate global CCS or DAC rates (or their sum) to an accuracy of around ±0.4 Pg C yr$^{-1}$ based on present capabilities, provided that an adequate ocean observing system is in place. A key element of such
Table 1. Modelled contributions to δAPO change from year 2010 to 2060 expressed on an annual basis, i.e. total change divided by 50 years. Units are in per meg per year.

<table>
<thead>
<tr>
<th></th>
<th>baseline scenario</th>
<th>CCS or DAC scenarios</th>
<th>target observational accuracya</th>
</tr>
</thead>
<tbody>
<tr>
<td>oceanic CO₂ uptake</td>
<td>−8.31</td>
<td>−7.88</td>
<td>±0.4b</td>
</tr>
<tr>
<td>fossil-fuel burning</td>
<td>−8.44</td>
<td>−8.44</td>
<td>±0.5c</td>
</tr>
<tr>
<td>capture process</td>
<td>0</td>
<td>−2.47</td>
<td>±0.8d</td>
</tr>
<tr>
<td>air–sea N₂ exchangee</td>
<td>0</td>
<td>0</td>
<td>±0.1f</td>
</tr>
<tr>
<td>air–sea O₂ exchangee</td>
<td>0</td>
<td>0</td>
<td>n.a.g</td>
</tr>
<tr>
<td>total (observable)</td>
<td>−16.75</td>
<td>−18.78</td>
<td>±0.4e</td>
</tr>
</tbody>
</table>

aRough estimate of feasible target, assuming an adequate observing system is in place.
bRequires direct determination by repeat hydrography; also accounts for uncertainty in air–sea O₂ exchange term.
cEstimated from contribution to ocean sink in table 5 of Manning & Keeling [18].
dEstimated from quadrature sum of other errors, as required to balance global budget, assuming an additional contribution of ±0.15 per meg yr⁻¹ from uncertainty in αB according to Manning & Keeling [18]. A precision of ±0.8 per meg yr⁻¹ corresponds to a resolution in the global capture rate of ±0.4 Pg C yr⁻¹.
eNeglected by model, but required for complete budget.
fBased on uncertainty in ocean warming rate according to Manning & Keeling [18].
gAs clarified by Keeling et al. [44], repeat hydrographic measurements will provide a more direct constraint on the relevant combined fluxes of O₂ and CO₂ than either separately.

an observing system is repeat hydrographic measurements to quantify temporal changes in dissolved O₂ and dissolved inorganic carbon species, which are directly related, at the global scale, to the relevant air–sea gas exchange terms.

5. Impact on interhemispheric gradient

Most fossil-fuel burning occurs in the northern extra-tropics. Given the approximate 1 year time scale for CO₂ in the northern extra-tropics to mix into the Southern Hemisphere (SH) via atmospheric circulation [45], an excess in the annual mean CO₂ concentration of around 7 ppm in the Northern Hemisphere (NH) relative to the SH is expected based on current emissions. The observed excess, however, is only approximately 3 ppm as a result of other processes, such as CO₂ uptake by the land and oceans as well as by the natural north–south transport of carbon by ocean circulation. Fossil-fuel burning also tends to cause deficits in O₂/N₂, δ¹³C and Δ¹⁴C in the NH compared with the SH, and the gradients in these tracers are also strongly influenced by land and oceanic exchanges.

Any widespread implementation of CCS would also necessarily occur mostly in the northern extra-tropics. CCS will change the gradients in CO₂, δ¹³C and Δ¹⁴C in a way that is essentially indistinguishable from that of reduced fossil-fuel burning. CCS would have no impact, however, on the O₂/N₂ gradient.

By reducing the CO₂ gradient but not the O₂/N₂ gradient, CCS will change the δAPO gradient, causing δAPO to decrease in the NH compared with the SH. Based on the 1 year interhemispheric exchange time and the atmospheric mass,
Table 2. Nominal exchange ratios for CO₂ source/sink processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>(\delta(O_2/N_2) : CO_2) (per meg ppm(^{-1}))</th>
<th>(\delta^{13}C : CO_2) (% ppm(^{-1}))(^a)</th>
<th>(\Delta^{14}C : CO_2) (% ppm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>fossil-fuel burning</td>
<td>-6.7</td>
<td>-0.045</td>
<td>-2.5</td>
</tr>
<tr>
<td>land biospheric sink</td>
<td>-5.2</td>
<td>-0.048</td>
<td>0</td>
</tr>
<tr>
<td>ocean sink</td>
<td>0</td>
<td>-0.005</td>
<td>0</td>
</tr>
<tr>
<td>isoflux</td>
<td>n.a.</td>
<td>(\infty)</td>
<td>(\infty)</td>
</tr>
<tr>
<td>carbon capture and storage</td>
<td>0</td>
<td>-0.045</td>
<td>-2.5</td>
</tr>
<tr>
<td>direct air capture</td>
<td>0</td>
<td>-0.013</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\)Estimates based on a CO₂ concentration of 400 ppm, and fractionation of \(-18\%\) and \(-5\%\) for the land sink and DAC, respectively.

The effect would decrease \(\delta APO\) in the NH relative to the SH by approximately 5 per meg for each Pg C of CCS in the northern extra-tropics. The \(\delta APO\) gradient has been measured over the past two decades to a precision of around \(\pm 2\) per meg [44,46,47]. The mean gradient is small (approx. 5 per meg NH deficit), but appears to have quasi-decadal variability at the \(\pm 5\) per meg level [44]. If the natural variability in the \(\delta APO\) gradient can be adequately understood, continued measurements could constrain hemispheric CCS rates to the level of \(\pm 0.4\) Pg C yr\(^{-1}\).

The \(\delta APO\) gradient would also be impacted by DAC, depending on its distribution. DAC does not need to be collocated with fuel usage, however, allowing a more uniform distribution between the hemispheres. In a world with both DAC and CCS, the \(\delta APO\) gradient will constrain the combined spatial distributions of CCS and DAC.

6. Discussion

Our goal was to examine the possibility of verifying rates of CCS via observed changes in the atmosphere, both in the near-field, i.e. within a few kilometres of processing plants and storage sites, and at global and hemispheric scales through multiple tracer measurements. Atmospheric detection of CCS (and leakage) appears feasible by exploiting differences in the exchange ratios (\(O_2 : C\), \(^{13}\)C/\(^{12}\)C and \(^{14}\)C/\(^{12}\)C) of CCS relative to other processes, as summarized in table 2. In the near field, for example, combined measurements of CO₂ concentration with measurements of \(O_2/N_2\) ratio and/or \(\delta^{13}C\) can help to resolve leakage or capture efficiency in the face of variability due to vegetation and soils. At the global scale, combined measurements of CO₂, \(O_2/N_2\), \(\delta^{13}C\) and \(\Delta^{14}C\) may provide constraints for understanding rates of CCS in relation to other processes, such as improvements that allow reduced fossil-fuel usage, DAC or land sequestration. On both scales, the most powerful constraint on CCS (or DAC) comes from combined measurements of CO₂ and \(O_2/N_2\). \(\delta^{13}C\) and \(\Delta^{14}C\) data can also provide useful constraints in many circumstances, but are more limited by measurement precision or smaller relative signals.
In the near field, detecting any CO₂ excess from leakage is only the first step. A critical additional step is to interpret the concentration changes in terms of fluxes, which requires some form of inverse modelling. This is an active field, and much progress can be expected in the near future [16]. Another critical step is to better define the O₂ : C and \(^{13}\)C/\(^{12}\)C exchange ratios of local ecosystems and their natural variability. This could be done as an integral part of a field programme, by placing field instrumentation in proximity to potential leakage sites and in nearby locations as controls. Based on present understanding of land ecosystem exchange ratios and available measurement technology, it would appear possible to detect CO₂ leakage to the level of approximately 2 ppm under a wide range of circumstances, even with active vegetation. In sites with less active vegetation, such as arid regions, even lower detection limits might be feasible. The ability to discriminate between leakage and ecosystem CO₂ exchanges opens the possibility to resolve emissions under near-stagnant conditions, when CO₂ excesses from all sources will build up to higher levels. This could be especially critical for leak detection and addressing issues of public safety. The ability to exploit O₂/N₂ and δ\(^{13}\)C measurements to resolve leakage hinges on the rapid progress that has been made over the past decade in field-deployable sensors for these species. Although Δ\(^{14}\)C measurements could also be useful for near-field CCS monitoring, present technology requires flask sampling, with high costs per data point.

Other processes besides land ecosystem exchange may produce atmospheric signatures that may interfere with the signatures of CCS in near-field applications. Fossil-fuel burning can occur in varying O₂ : C ratios, depending on fuel type, and this may cause variability in many settings, particularly in urban or industrial areas. Cement manufacture, which releases CO₂ produced via thermal decomposition of limestone, may interfere in some settings. Increased use of hydrogen gas (H₂) as an energy carrier, e.g. derived ultimately from fossil fuels, will alter patterns of CO₂ production and O₂ consumption from fossil fuels by separating the point of CO₂ production (associated with H₂ production) from the O₂ consumption (associated with energy end use). Hydrogen usage cannot affect global CO₂ and O₂ budgets, however, because it does not alter the total O₂ consumed and CO₂ produced.

At global and hemispheric scales, the signature of CCS will be superimposed on other processes impacting CO₂, O₂/N₂, δ\(^{13}\)C and Δ\(^{14}\)C. How to make best use of observations of these parameters will depend on which processes are best known from independent information. Our analyses suggest that, with present uncertainties in fossil-fuel emissions, and assuming an improved ocean observing system is implemented, it should be feasible to detect global and hemispheric rates of CCS via the tracer δAPO to the \(±0.4\) Pg C yr\(^{-1}\) level. The observations would constrain, not the gross capture rate, but the net rate, discounting leakage, which is the appropriate measure for assessing the effectiveness of CCS in reducing CO₂ buildup in the atmosphere. If both CCS and DAC are implemented on a wide scale, the observations would constrain the combination of both processes. Obtaining a detection limit near \(±0.4\) Pg C yr\(^{-1}\) will require independent development of an ocean observing system and maintaining the current accuracy in estimating fossil-fuel emissions, despite financial incentives for fraud. In the absence of an adequate ocean observing system or with degraded fossil-fuel estimates, δAPO measurements would serve to constrain the combined exchanges from CCS, the oceans and fossil-fuel burning, but not each separately.
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