REVIEW

Non–CO$_2$ greenhouse gases and climate change

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Earth's climate is warming as a result of anthropogenic emissions of greenhouse gases, particularly carbon dioxide (CO$_2$) from fossil fuel combustion. Anthropogenic emissions of non–CO$_2$ greenhouse gases, such as methane, nitrous oxide and ozone-depleting substances (largely from sources other than fossil fuels), also contribute significantly to warming. Some non–CO$_2$ greenhouse gases have much shorter lifetimes than CO$_2$, so reducing their emissions offers an additional opportunity to lessen future climate change. Although it is clear that sustainably reducing the warming influence of greenhouse gases will be possible only with substantial cuts in emissions of CO$_2$, reducing non–CO$_2$ greenhouse gas emissions would be a relatively quick way of contributing to this goal.

Greenhouse gases (GHGs) alter Earth's climate by absorbing energy in the lower atmosphere and re-emitting it. Although anthropogenic emissions of CO$_2$ contribute most to GHG-induced warming, several other gases, such as methane (CH$_4$), nitrous oxide (N$_2$O), ozone-depleting substances (ODSs), hydrofluorocarbons (HFCs), sulphur hexafluoride (SF$_6$) and perfluorocarbons (PFCs), also affect climate for decades to millennia after being emitted. Because most anthropogenic emissions of these non–CO$_2$ GHGs are linked to society's fundamental needs for food and energy, they will continue to increase and further warm the climate unless substantial efforts are undertaken to reduce them worldwide[1–4]. Significant opportunities to mitigate anthropogenic emissions of these gases exist, although some will be easier to exploit than others[2,5–8]. By quantifying emissions associated with different human activities and expressing those emissions on a CO$_2$-equivalent basis, climate benefits can be linked with specific mitigation targets.

Here we review human activities and natural processes that emit non–CO$_2$ GHGs, and explore the time-dependent responses of the warming influence (also called climate forcing or radiative forcing) of these chemicals to emissions reductions. Large cuts in anthropogenic emissions of both long- and short-lived GHGs could stabilize climate forcing fairly rapidly, though the exact impacts of such cuts are uncertain because of feedbacks between climate change and GHG emissions from natural processes. Improving our understanding of these feedbacks and our ability to quantify anthropogenic and natural GHG fluxes on regional and global scales could help in assessing mitigation efforts and ensure their success in diminishing future climate warming.

Sources and sinks of non–CO$_2$ gases

Overall changes in emissions

The influence of an emitted GHG on future climate is estimated from its ability to absorb available infrared radiation and its persistence in the atmosphere. The global warming potential (GWP) of a GHG emission is this climate influence, integrated over time and expressed relative to the climate influence of an equivalent mass of CO$_2$ emission (Box 1). Multiplying emission amounts by 100-yr GWPs allows estimates of 'CO$_2$-equivalent' (CO$_2$-eq) emissions. This approach has a number of limitations[9] but does provide a means of comparing time-integrated climate impacts arising from emissions of different GHGs.

During the 1980s, human-derived, non–CO$_2$ GHG emissions were comparable in sum to CO$_2$ emissions from fossil fuel combustion

($\sim$20 Gt CO$_2$-eq yr^{-1} from each; Fig. 1). Since 1990, total emissions of non–CO$_2$ GHGs have declined to 15 Gt CO$_2$-eq yr^{-1}, mainly due to reductions in ODSs as agreed to in the Montreal Protocol on Substances that Deplete the Ozone Layer[10,11] (henceforth the Montreal protocol). For a time these reductions were sufficient to offset increases in emissions of other GHGs, but since 2003 continued increases in fossil fuel CO$_2$ have exceeded those offsets. In 2008, the 15 Gt CO$_2$-eq yr^{-1} contribution from non–CO$_2$ GHGs accounted for 30% of all human-related long-lived greenhouse gas (LLGHG) emissions (total anthropogenic CO$_2$ emissions were $\sim$35 Gt CO$_2$ yr^{-1} in 2008[12]; data available at http://lgmacweb.env.uea.ac.uk/lequere/co2/carbon_budget.htm; Fig. 1). In this section, we review natural and anthropogenic sources and sinks of non–CO$_2$ GHGs and the potential for their magnitudes to change with climate.

Methane

At $\sim$1.8 p.p.m. (parts per million as mole fraction in dry air; refs 13, 14), CH$_4$ is the most abundant non–CO$_2$ GHG in the atmosphere today. Its present atmospheric mole fraction is 2.5 times higher than that observed in ice cores dated to AD 1000–1750 and is higher than that observed throughout the existing ice-core record, which spans the past 800,000 yr (refs 15, 16). Methane's atmospheric increase since 1750 implies anthropogenic emissions of 340 $\pm$ 50 Tg CH$_4$ yr^{-1} (8.5 $\pm$ 1.3 Gt CO$_2$-eq yr^{-1}; uncertainty, 1 s.d.), or nearly two-thirds of present total emissions, assuming a constant lifetime[1,17,18] (Fig. 2 and Box 1). Agriculture and fossil fuel exploitation together account for about 230 Tg CH$_4$ yr^{-1} (5.8 Gt CO$_2$-eq yr^{-1}), or two-thirds of all human-derived CH$_4$ emissions; smaller emissions arise from waste treatment (landfills, manure and sewage) and biomass burning. The contribution of wetlands dominates natural CH$_4$ emissions (150–180 Tg CH$_4$ yr^{-1}; refs 17, 18) and is highly sensitive to variations in temperature and water table height[19]. Most wetland emissions ($\sim$70%) come from the tropics[17,18] and are enhanced during warm, wet periods. Smaller amounts of CH$_4$ are emitted from oceans and by termites (combined contribution of $\leq$45 Tg CH$_4$ yr^{-1}; refs 1, 17, 18).

Methane has a shorter steady-state lifetime ($\sim$9 yr) than most other LLGHGs[20], and its loss is primarily the result of atmospheric oxidation by the hydroxyl radical (OH$^\bullet$). This sink links the abundance of CH$_4$ to the complex atmospheric chemistry that influences OH$^\bullet$ concentrations ([OH$^\bullet$]) on a global scale and creates a positive feedback between CH$_4$

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Estimating GHG emissions

A successful mitigation strategy must include the means to quantify emissions and their changes and include the ability to attribute changes in emissions to specific processes, be they natural or anthropogenic. Emissions are estimated using different methodologies.

• Inventory-based, 'bottom-up' accountings of activities resulting in emissions are multiplied by appropriate emission factors. GHG emissions reported to the United Nations Framework Convention on Climate Change are derived from inventory-based accountings that have a range of accuracies. These inventories are based on an incomplete understanding of emissive processes, have uncertainties that are difficult to quantify and typically are updated infrequently.

• Atmosphere-based studies involve inferring flux magnitudes on local to global scales on the basis of measured atmospheric mixing ratio changes and gradients, their time-dependent variations, and covariations with meteorological parameters or other trace gases. These 'top-down' approaches have historically provided estimates of total global fluxes and can provide independent assessments of global, inventory-based emission magnitudes. Significant discrepancies have been identified[7,61,63,91] between bottom-up and top-down global estimates, highlighting uncertainties in both methods. Recent advances in measurement technologies and high-resolution transport models have made it possible to calculate regional estimates of emissions from top-down analyses[43,44,92–96]. These approaches may provide an independent means to assess or verify regional or national bottom-up emission inventories but at present have substantial uncertainties.

• Process-based approaches provide an understanding of the mechanisms involved in generating GHG emissions and the sensitivities of these mechanisms to changes in climate-related variables such as temperature and precipitation. Knowledge gained from process studies can improve both bottom-up and top-down methodologies.

Emissions are expressed, for example for CH_4, in units of teragrams of CH_4 per year, where 1 Tg CH_4 is equivalent to 1×10^{12} g CH_4, 0.75×10^{12} g C and 0.00075 Gt C. Emissions are multiplied by 100-yr GWPs updated in the most recent climate assessment[9] (25 for CH_4, 298 for N_2O, 133–14,400 for commonly used ODSs and HFCs, and 7,000–23,000 for PFCs, NF_3 and SF_6) to give the CO_2-eq emissions reported here. With this equivalence, an emission of 100 Tg CH_4 corresponds to 2.5 Gt CO_2-eq. One-hundred-year GWPs adopted by the United Nations Framework Convention on Climate Change are based on previous scientific assessments[47] and would give CO_2-eq CH_4 emissions 16% smaller, CO_2-eq N_2O emissions <0.7% larger and total emissions from other non-CO_2 GHGs ~4% smaller than those estimated here.

Figure 1 | Anthropogenic emissions of non-CO_2 GHGs and CO_2.
Anthropogenic emissions of non-CO_2 GHGs are calculated as the difference between total emissions derived from observed mixing ratio changes in the global background atmosphere with constant steady-state lifetimes[9,56] and a constant natural background[9,10,13,33,56]. As a result, any variations in natural fluxes are included in the values presented. To reduce the influence of natural variability on our ability to discern decadal changes, emissions of CH_4 and N_2O were smoothed by averaging over 4-yr periods. By the end of 2008, emissions of CFCs (predominantly from halocarbon banks in recent years; dashed grey line) accounted for just over half of total ODS emissions (CFCs plus HCFCs; solid grey line). Emissions of CO_2 from fossil fuel exploitation (ff) and from fossil fuels plus land use change (ff + lu) are from bottom-up inventories[12]. Weighting factors used here to derive CO_2-eq emissions (100-yr global warming potentials) are from ref. 9 (Box 1). Emissions too small in 2008 to be visible on this scale include[9,63,64] SF_6 (~0.17 Gt CO_2-eq yr^{-1}), PFCs (~0.1 Gt CO_2-eq yr^{-1}) and NF_3 (~0.01 Gt CO_2-eq yr^{-1}).

and its own abundance; increased CH_4 is expected to decrease [OH•] and lead to a longer CH_4 lifetime. Reduced [OH•] would also mean longer lifetimes and enhanced climate influences for HFCs and hydrochlorofluorocarbons (HCFCs), decreased conversion of SO_2 to sulphate aerosol (less cooling) and changes in the cycling of tropospheric ozone, which is a powerful, very short-lived GHG[9,21,22]. Very short-lived substances (for example NO_x and tropospheric ozone, which have lifetimes of days to months) can still affect climate forcing on longer timescales through their influence on [OH•] and, therefore, CH_4 (ref. 22).

In the absence of substantial mitigation efforts, both anthropogenic and natural emissions of CH_4 are likely to increase in the twenty-first century as global population increases and climate warms. Inventory-based estimates indicate a substantial increase in human-derived CH_4 emissions in recent years (10% from 2000 to 2005), for example, due to rapid economic growth and increasing demand for food and energy,
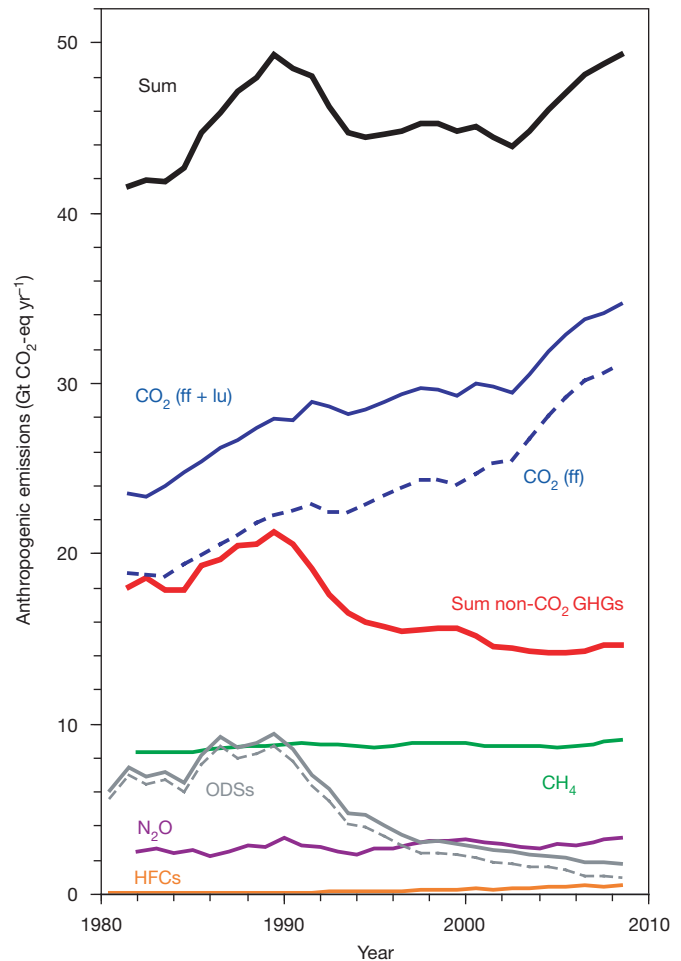
primarily in Asia[23]. Surprisingly, the observed global annual mean atmospheric abundance of CH_4 was nearly constant during this period[13,14] (varying by <0.4% from 1999 to 2006), implying inaccurate inventories, simultaneous offsetting decreases in natural emissions or a comparable increase in [OH•]. A top-down inverse modelling analysis of global CH_4 observations from 1984 to 2003 also suggests a small increase in total anthropogenic emissions in the early 2000s offset by decreasing natural sources[17], although these results are not independent of the inventory emissions and their uncertainties used to initialize the model (primarily because of limited available observations).

The sensitivity of natural CH_4 emissions from wetlands to warmer, wetter climates suggests a positive feedback between emissions and climate change that is apparent in ice-core records[15,16]. Although the magnitude of this feedback is uncertain, it could be substantial; modelling of the wetland response to a doubling of CO_2 (corresponding to a global temperature change of 3.4 °C) resulted in an increase in wetland
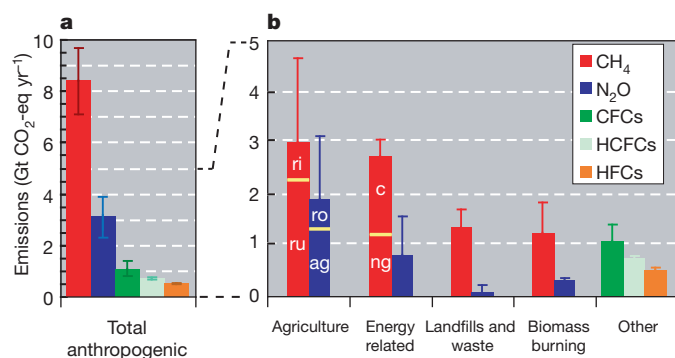
Figure 2 | Annual anthropogenic emissions of non-CO_2 GHGs in recent years[1,9,10,17,18,56]. **a**, Emissions by compound. Uncertainties reflect one standard deviation (s.d.) of estimates[10,17,56], and for N_2O are calculated as the difference between total emissions derived from background atmospheric changes[1] and emissions needed to sustain late-Holocene mixing ratios of 255–270 p.p.b. (refs 15, 32), assuming an uncertainty in lifetime of $\pm5\%$. **b**, Emissions by compound and sector (note scale change). Emissions associated with different sources within each main sector are derived from inventory- and atmosphere-based analyses (Box 1). For CH_4, ruminants (ru, 2.3 ± 1.0 Gt CO_2-eq yr^{-1}); rice agriculture (ri, 0.8 ± 0.7 Gt CO_2-eq yr^{-1}); natural gas, oil and industry (ng, 1.6 ± 0.3 Gt CO_2-eq yr^{-1}); and coal mining (c, 1.2 ± 0.2 Gt CO_2-eq yr^{-1}) are the main contributors. Values for CH_4 indicate the mean and 1 s.d. of all model estimates in table 7.6 of ref. 1. Emissions of N_2O are from agriculture directly (ag, 1.3 (0.8–2.2) Gt CO_2-eq yr^{-1}) and from run-off (ro, 0.6 (0.2–0.9) Gt CO_2-eq yr^{-1}) to aquatic ecosystems of excess nitrogen attributable to agriculture[1] (derived as 75% of total nitrogen in run-off[90]). Energy-related N_2O emissions[1] represent the total from fossil fuel combustion and industrial processes (0.33 (0.1–0.8) Gt CO_2-eq yr^{-1}), atmospheric deposition (0.28 (0.14–0.42) Gt CO_2-eq yr^{-1}) and the remaining excess anthropogenic nitrogen reaching aquatic regions from run-off (0.2 (0.06–0.3) Gt CO_2-eq yr^{-1}; 25% of total[90]). Uncertainties quoted here for N_2O are ranges derived from table 7.7 of ref. 1. Total emissions of CFCs (1.0 Gt CO_2-eq yr^{-1}), HCFCs (0.7 Gt CO_2-eq yr^{-1}) and HFCs (0.5 Gt CO_2-eq yr^{-1}) and the indicated uncertainties (1 s.d.) are derived for 2008 from top-down methods[10,56]. Although total biomass burning emissions are included here[1,9,56] (1.3 Gt CO_2 as CH_4 and 0.3 Gt CO_2 as N_2O), a small fraction of that burning is natural. In **b**, uncertainties shown represent only those associated with the total by compound for each sector.

emissions of CH_4 equal to about one-third of present anthropogenic emissions of CH_4 (ref. 24). In addition, Arctic permafrost contains ~1,000 Gt of carbon (Gt C) in its top 3 m, and some of this carbon could be converted to CH_4 by microbes as permafrost melts, depending on the height of the water table[25]. Given the large size of this reservoir, small increases in the release of this carbon as CH_4 as the Arctic warms could substantially augment natural CH_4 emissions. The Arctic Ocean contains an additional 30,000–170,000 Tg CH_4 (20–130 Gt C) in sedimentary clathrates on the relatively shallow continental shelves, although this potential source is unlikely to become important in the short term[26,27]. An additional natural CH_4 source from plants was recently proposed[28] but is probably insignificant[29].

The near-constant global mixing ratios during 1999–2006 were unexpected, and the next surprise concerning CH_4 was observed in 2007 when its global concentration began increasing again[13,14]. Updated measurements[13] show that this increase is ongoing, at a mean rate during 2007–2010 of ~6 p.p.b. yr^{-1} (p.p.b., parts per 10^9 as mole fraction in dry air). Assuming no change in the lifetime of CH_4, these observations correspond to global emissions during 2007–2010 that were ~17 Tg CH_4 yr^{-1} larger, on average, than in the previous eight years, and they bring up an important question: is this abrupt increase the result of changes in natural processes, human alterations of the natural system or an increase in direct anthropogenic emissions? In the absence of updated inventory estimates, results from global atmospheric observations[13,14] have provided some initial clues as to the causes of the 2007 and 2008 increases. Whereas in 2007 CH_4 mixing ratios increased most rapidly at polar northern latitudes and in the Southern

Hemisphere, in 2008 they increased most rapidly in the tropics, with near zero growth in the Arctic[13]. These observations argue against these mixing ratio increases arising from direct anthropogenic emissions, which would tend to create enhancements in the low- to mid-latitude Northern Hemisphere.

Attributing recent increases to specific CH_4 sources or sinks becomes more definitive with measurements of additional trace gases and related variables. Measurements of CH_4 isotopologues (for example $^{13}CH_4$) contain information about CH_4 sources because these sources can enrich or deplete the ^{13}C or ^2H content of atmospheric CH_4. Methane measured at Alert, Canada, in the summer of 2007 was depleted in ^{13}C, suggesting an enhanced wetland source in northern high latitudes[13]. Carbon monoxide, ethane and CH_3Cl are co-emitted with CH_4 from biomass burning, but measurements of these chemicals suggest no significant enhancements during 2007–2008. Measurements of trace gases oxidized by OH$^\bullet$ (for example methyl chloroform) suggest that [OH$^\bullet$] decreases may explain only a portion of the CH_4 enhancements measured in 2007[13,14,30]; changes in [OH$^\bullet$] after 2007 have not yet been published. Taken together, the evidence suggests that the renewed increases in atmospheric CH_4 observed during 2007 and 2008 arose primarily from enhanced natural wetland emissions as a result of anomalously high temperatures in the Arctic and greater than average precipitation in the tropics associated with a persistent La Niña[13]. The causes of the continued increases in 2009 and 2010 are not yet clear, but may be related to the strong La Niña that started in early 2010.

Nitrous oxide

At 322 p.p.b., the atmospheric N_2O concentration is at present 19% higher than pre-industrial levels[15,31,32] and has increased at a mean rate of 0.7 p.p.b. yr^{-1} during the past 30 yr (refs 9, 33; data from ref. 33 updated at http://www.esrl.noaa.gov/gmd/aggi/). Nitrous oxide concentrations in the pre-industrial atmosphere reflect the balance between production due primarily to biogeochemical cycling of nitrogen and slow stratospheric losses. Humans have augmented nitrogen cycling through the use of inorganic fertilizer, cultivation of nitrogen-fixing crops, and deposition of NO_x from combustion of fossil fuels[5]. These processes increase the availability of mineralized nitrogen (for example NH_4^+ and NO_3^-) and lead to N_2O emissions through microbially mediated nitrification or denitrification in both terrestrial and aquatic ecosystems[5,34,35]. Only a small fraction of applied or deposited anthropogenic reactive nitrogen is ultimately emitted as N_2O, although this fraction accounts for the largest anthropogenic source of N_2O and is sensitive to climate, agricultural practices, and the availability of oxygen and nutrients[1,5,34–42]. Other anthropogenic activities such as fossil fuel combustion, industrial processes (for example the production of adipic and nitric acids), biomass burning and waste management release N_2O directly (Fig. 2).

Anthropogenic N_2O emissions at present account for 6.7 ± 1.7 Tg N yr^{-1} (3.1 ± 0.8 Gt CO_2-eq yr^{-1}; uncertainty, 1 s.d.), or about 40% of all N_2O emissions, and arise primarily from agricultural activities (1.9 Gt CO_2-eq yr^{-1}) and industrial processes including fossil fuel combustion[1] (0.8 Gt CO_2-eq yr^{-1}; Fig. 2). Natural N_2O sources are predominantly terrestrial (~75%), and these emissions are highest in the tropics[43,44]; natural marine sources typically are strongest in upwelling regions[45].

Nitrous oxide is removed from the atmosphere much more slowly than CH_4, given its steady-state lifetime of about 120 yr (refs 46, 47); less than 1% of atmospheric N_2O is removed annually from the atmosphere, primarily by photolysis and oxidative reactions in the stratosphere. The lifetime of N_2O may change in the future as it is sensitive to air transport rates through the stratosphere[48] and to stratospheric ozone abundance[49], but the effects of these processes are poorly quantified or are expected to be small. Nitrous oxide is also destroyed (and produced) by denitrification in nearly anoxic environments and, possibly, as recently suggested, by an uncharacterized process in forest soils under drought[50]; again, however, the influence of these processes on the lifetime of N_2O is probably small[51].

How might anthropogenic N_2O emissions change in the future? An inventory analysis[23] suggests increases in N_2O emissions of ~5% per decade from 1979 to 2005. This is comparable to the increase, ~7% per decade, inferred for anthropogenic emissions from the observed global increase. This increase is likely to continue in the absence of mitigation efforts[2,4,5], given that most emissions of N_2O are associated with feeding the world's growing population. Furthermore, enhanced use of fertilizer to cultivate biofuel crops could increase N_2O emissions and offset some of the climate benefits anticipated from biofuels[36–38]. A large fraction of the nitrogen used in agriculture is typically lost to the environment, suggesting that more judicious application of fertilizer could decrease future N_2O emissions without impacting crop yields. Further N_2O mitigation strategies involve increasing nitrogen uptake efficiency by crops, expanding the use of nitrification inhibitors, improving manure management strategies and expanding access to sewage treatment[5,6,8,52].

Future changes in natural emissions of N_2O are also possible, given ice-core records suggesting that climate change might affect both marine and terrestrial emissions on short and long timescales[15,31,32,41]. Emissions of N_2O from soils in their natural state or soils influenced by humans are sensitive to temperature, hydrology, drought cycles and also land use change[1,5,39–42,50,53,54]. Inversion studies have confirmed the importance of tropical N_2O sources between the equator and $30° N$, and suggest possible emission increases from this region over time[43,44], although signals are small relative to the present measurement precision and can be dominated by other atmospheric processes such as stratosphere–troposphere exchange[43,44,55]. As is also true for CH_4, sensitivities of emissions and loss to natural processes put increased demands on our understanding of regional N_2O budgets in atmosphere-based, top-down inversion studies of emissions, as they make changes in the natural system that are difficult to distinguish from those related to human mitigation efforts.

Montreal protocol gases and substitutes

Unlike CH_4 and N_2O, most ODSs that influence climate have no significant natural sources. Total aggregate emissions of primary ODSs (CFCs, carbon tetrachloride, methyl chloroform, methyl bromide and halons) have decreased from ~9 to $1 Gt CO_2$-eq yr^{-1} since the late 1990s because of adherence to the Montreal protocol (Figs 1 and 2). Global atmospheric concentrations of nearly all these chemicals have declined in recent years as a result[56]. Substitutes for the primary ODSs (that is HCFCs, which are also ODSs controlled by the Montreal protocol, and the non-ozone-depleting HFCs that are included in the Kyoto Protocol) are also potent GHGs. Their global concentrations and emissions have increased in recent years[7,9–11,56]. During 2008, emissions of HCFCs amounted to $0.7 Gt CO_2$-eq yr^{-1} and emissions of HFCs totalled $0.5 Gt CO_2$-eq yr^{-1} (Figs 1 and 2).

Although the Montreal protocol's controls on future HCFC production were strengthened recently[10], future climate impacts of ODSs and HFCs are uncertain for three reasons. First, although HFCs are included in the Kyoto Protocol, their atmospheric burden and, consequently, their radiative forcing could increase substantially owing to their increased use as ODS replacements, particularly in developing countries[10,11]. The future climate impact of HFCs will depend on emission magnitudes and on the extent to which alternatives with shorter lifetimes and lower GWPs are adopted. There is also concern over emissions of HFC-23, a potent GHG created as an unintended by-product during HCFC-22 production. Emission of HFC-23 has the potential to increase in the future in part because only a portion of the HFC-23 is at present destroyed through the Clean Development Mechanism projects[57,58] of the United Nations Framework Convention on Climate Change. Second, halocarbon 'banks', that is, reservoirs of produced but not yet emitted chemicals, are a substantial present source. Most chemicals in banks will ultimately escape to the atmosphere unless destroyed. Although global halocarbon banks of CFCs, HCFCs and HFCs were ~$19 Gt CO_2$-eq in 2005, only a portion is likely to be recoverable[7]. In the United States, for example, about 25% of the 2005 halocarbon bank was classified as 'accessible', that is, in forms

found in fire extinguishing, refrigeration or air conditioning appliances, which are more easily recoverable than, for example, foams[7]. Banks of HCFCs in developing countries and HFCs in developed countries have probably increased in recent years owing to dramatically increased production[7,10]. Third, potential systematic trends in global [OH•] (for example from changes in CH_4, carbon monoxide, NO_x, tropospheric ozone and water vapour[20,21,59]) would affect HCFC and HFC lifetimes and their time-integrated climate impacts.

Extremely long-lived gases

A number of chemicals with extremely long lifetimes and small or insignificant natural sources are observed at very low mixing ratios in the
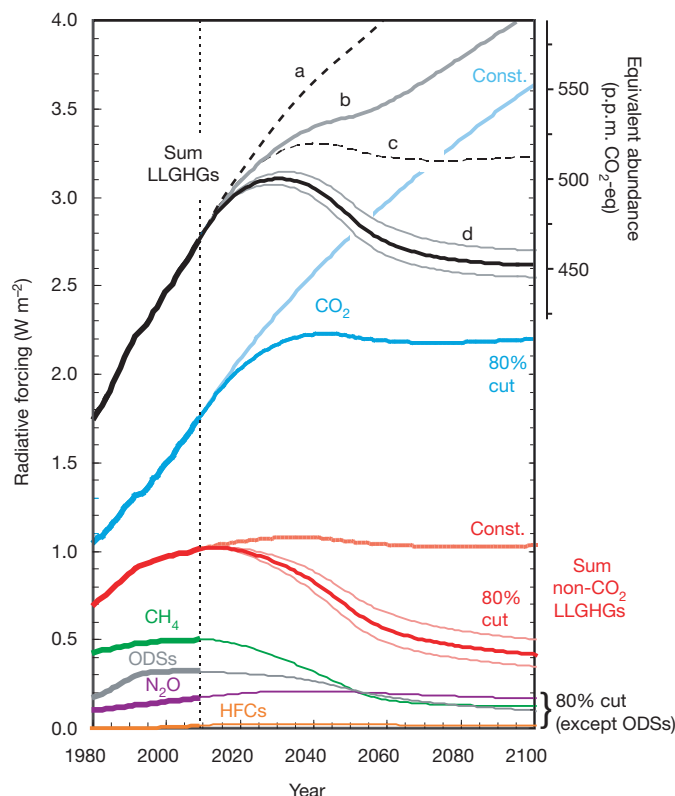

Figure 3 | Direct radiative forcing derived from observed and projected abundances of LLGHGs[33]. Projections are from different emissions scenarios: constant future emissions at 2008 levels; 80% cuts in those emissions, phased in linearly between 2009 and 2050 (and constant thereafter); and, for ODSs, emissions based on existing controls supplied by the Montreal protocol[10]. Future forcing from the sum of all LLGHGs (black lines) is shown for constant future emissions (line 'a'), constant future CO_2 emissions but an 80% decrease in non-CO_2 LLGHG emissions (line 'b'), an 80% decline in CO_2 emissions but constant future non-CO_2 LLGHG emissions (line 'c') and 80% reductions in emissions of all LLGHGs including CO_2 (line 'd'). These sums are derived from changes in CO_2 (blue lines) and the sum of non-CO_2 LLGHGs (red lines). Results for individual non-CO_2 GHGs and groups of them are also shown. Uncertainties shown for selected projections (line 'd' and red line '80% cut') reflect a linear change in [OH•] of ±15% from 2009 to 2050 (based in part on the sensitivity of [OH•] to CH_4 changes[21,22]). The small feedback between N_2O abundance and its lifetime, and the small influence of CH_4 abundance on the N_2O lifetime, were not considered[46]. Future non-CO_2 GHG mixing ratios were calculated with a one-box model, whereas future CO_2 mixing ratios were calculated using the response function for a pulsed emission decay based on the Bern carbon cycle model[9] (Bern2.5CC). Projections presume constant natural emissions and losses, and thus do not include the potentially significant changes in natural emissions or non-OH• losses discussed in the text. For a given emissions scenario, future CO_2 abundances have additional uncertainties arising from potential changes in uptake by the land and ocean due to the influence of nitrogen availability (see text), climate change, increasing CO_2 concentration and ocean acidification[1,77–80]. Direct radiative forcings from PFCs ($0.005 W m^{-2}$), SF_6 ($0.004 W m^{-2}$) and NF_3 ($0.0001 W m^{-2}$) are too small in 2009 to be visible.

atmosphere today. Changes in climate due to emissions of these chemicals, however, are irreversible on millennial timescales[60]. Examples include SF_6, SF_5CF_3, nitrogen trifluoride (NF_3) and PFCs (CF_4, C_2F_6, C_3F_8 and so on). Recent atmospheric changes and inventory estimates[9,56,61–64] indicate fairly small CO_2-eq emissions of these gases as compared with other LLGHGs (Fig. 1), although emissions for most are increasing, necessitating continued monitoring to ensure that their climate forcings remain small. This is particularly true for gases that could increase substantially with increased electricity use (that is, SF_6) and for gases not included in existing international protocols (for example NF_3). Nitrogen trifluoride has received use recently in the electronics industry as a substitute for PFCs owing to climate concerns related to PFCs, and it is largely destroyed during the manufacturing process. Yet the NF_3 that does escape has a larger GWP than the PFCs it replaces[63].

Climate forcing from non-CO_2 gases

The direct climate forcing of a trace gas is proportional to its global concentration change since 1750 and how efficiently it absorbs available infrared radiation (its radiative efficiency as watts per square metre per p.p.b.). By 2009, the increase since 1750 in long-lived, non-CO_2 GHGs contributed a direct radiative forcing of $1.0\ W\ m^{-2}$, or 57% of that from CO_2 (Fig. 3). The concurrent increase in CH_4 accounted for half of this direct climate forcing ($0.5\ W\ m^{-2}$), that in ODSs accounted for about a third ($0.32\ W\ m^{-2}$) and that in N_2O contributed most of the remainder[33] ($0.17\ W\ m^{-2}$). Smaller forcings ($<0.02\ W\ m^{-2}$) stem from increases in HFCs, PFCs, SF_6 and NF_3 (Fig. 3).

Increases in CO_2 dominated the change in direct radiative forcing from all LLGHGs ($0.159\ W\ m^{-2}$) from mid 2004 to mid 2009; the increase in direct radiative forcing from the sum of all non-CO_2 GHGs was only 20% as large (Fig. 3). Increases in N_2O ($0.012\ W\ m^{-2}$), CH_4 ($0.006\ W\ m^{-2}$) and HFCs ($0.006\ W\ m^{-2}$) account for most of the change in radiative forcing attributable to non-CO_2 GHGs during this recent five-year period. Increases in direct radiative forcing from SF_6, PFCs and NF_3 were smaller ($<0.001\ W\ m^{-2}$ each), and no net change was observed in direct radiative forcing from ODSs, as increases in HCFCs ($0.008\ W\ m^{-2}$) were offset by comparable decreases in CFCs during this same period.

Some non-CO_2 GHGs also influence climate indirectly. For example, increased atmospheric CH_4 enhances stratospheric water vapour and tropospheric ozone, and also affects aerosols[22,65,66]. Including these indirect influences augments the present climate forcing of CH_4 from ~0.5 to $0.8–1.0\ W\ m^{-2}$ (refs 9, 22, 67). Human-derived, short-lived reactive nitrogen (for example NO_x) affects aerosol abundances, tropospheric ozone, global [OH•] and, therefore, atmospheric lifetimes of CH_4, HCFCs and HFCs[22]. During the past century, enhanced OH• production from increases in anthropogenic NO_x may have offset increased OH• losses due to higher concentrations of carbon monoxide and CH_4 (ref. 59). Decreases in stratospheric ozone, mostly from enhanced abundances of ODSs, have caused a climate forcing of $-0.05 \pm 0.1\ W\ m^{-2}$ (ref. 9; uncertainty, 90% confidence interval). Including these indirect influences suggests a net climate forcing in 2009 from non-CO_2 GHGs that is $0.2–0.4\ W\ m^{-2}$ higher than when only direct influences are considered.

Managing climate forcing with non-CO_2 gases

Without substantial mitigation efforts, emissions of non-CO_2 GHGs will probably increase as needs for energy and food increase globally and developing countries continue to modernize[2–5]. An average projected increase of ~50% for emissions of CH_4 and N_2O by 2050[2,68] (relative to 2000 values) and larger relative increases for HFCs[3,4,10,11,69] correspond to the emission of an additional ~10 Gt CO_2-eq yr^{-1} by 2050. Decreases of ~2 Gt $CO_2\ yr^{-1}$ are expected for ODS emissions by 2050 with continued adherence to controls set by the Montreal protocol[10]. Considered together, such emissions changes could cause direct climate forcing from all long-lived, non-CO_2 GHGs to reach ~1.5 W m^{-2} by 2050 (a 50% increase over their direct radiative forcing today).

To what extent could reductions of non-CO_2 GHG emissions affect climate forcing during the next 50–100 yr? A 25% reduction in anthropogenic emissions, phased in during 2009–2020, illustrates the range of sensitivities GHG concentrations have to emission reductions owing to their different lifetimes. Reducing anthropogenic emissions of all non-CO_2 GHGs in this manner would cause total radiative forcing from these gases to peak during the next decade (Fig. 4). This turnover stems primarily from declines in CH_4 concentration and demonstrates how CH_4 emissions reductions could offset a portion of the increases in radiative forcing from longer-lived GHGs on fairly short timescales. Methane's large influence and rapid response stems from its relatively short lifetime (~9 yr), its near balance of present total emissions and losses, and its large contribution to present climate forcing. This influence depends on the stability of atmospheric [OH•] (Fig. 3), although [OH•] is thought to be buffered against large changes; increases (or decreases) in both CH_4 and NO_x, for example, have offsetting influences on [OH•] (refs 21, 30, 59). By contrast, a 25% drop in emissions of N_2O or CO_2 only slightly slows the increase in radiative forcing from each of these long-lived gases, for which present total emissions substantially exceed losses (Fig. 4).

Reversing continued increases in radiative forcing from all LLGHGs will require much larger emissions reductions. An 80% reduction in anthropogenic emissions of CO_2 is required just to stabilize its direct radiative forcing[70] (Fig. 3). Such a large relative decrease is needed because CO_2 in today's atmosphere is long lived[9,71] and because its present total emissions far outweigh losses. Provided that non-CO_2 GHG emissions were also to remain constant, this 80% cut in CO_2 emissions could eventually stabilize climate forcing from all LLGHGs (Fig. 3, line 'c'). By contrast with the time response of CO_2, an 80% reduction in emissions of all non-CO_2 GHGs by 2050 would cause their radiative forcing to decrease substantially, not just stabilize, mainly owing to the rapid response of CH_4 to emissions decreases. When combined with similar relative cuts in CO_2 emissions, the direct radiative forcing from the sum of all LLGHGs actually peaks and begins decreasing well before 2050 (Fig. 3, line 'd'). But a sustained stabilization of climate forcing cannot be achieved with cuts in only non-CO_2 GHGs (Fig. 3, line 'b').
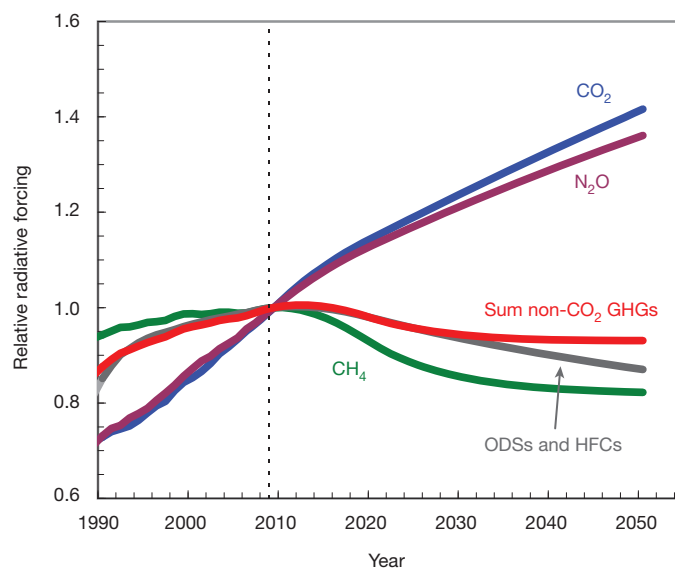

Figure 4 | Relative changes in radiative forcing from a 25% cut in GHG emissions. Radiative forcing expressed as a fraction of the forcing in 2009. Past forcings are based on measured mixing ratios as in Fig. 3. Future forcings are calculated assuming a 25% decline in 2008 emissions, phased in linearly between 2009 and 2020; emissions are kept at 2020 rates thereafter. Projections are made with techniques described in Fig. 3. This illustrative scenario represents an 11% decrease, relative to 1990 levels, in total anthropogenic emissions of GHGs included in the Kyoto Protocol (that is, not ODSs).

A 50–80% cut in CO_2 emissions by 2050 (relative to 1990) has been discussed as a means to limit GHG abundance to <500 p.p.m. CO_2-eq and mean, global temperature increases to 2–2.4 °C above pre-industrial values[2,70,72]. Such large cuts in CO_2 emissions would probably require substantial changes to future energy production. We considered comparable reductions in non-CO_2 GHG emissions here primarily to demonstrate rough upper limits to and the timescales of climate forcing benefits associated with large cuts in their emissions. Although emissions of non-CO_2 GHGs could be reduced substantially with minimal net cost given present technologies[5,8,68] (40% cuts in CH_4, 10–15% cuts in N_2O and ~40% cuts in gases containing fluorine, relative to 2010 values[73]), achieving larger cuts in emissions will depend on cost incentives (for example the price of carbon) and future technological advances[2,68]. Multifaceted modelling analyses that consider abatement costs, mitigation potentials and their potential future evolution demonstrate that a multi-gas approach to stabilizing radiative forcing reduces the required initial cuts in CO_2 emissions and achieves stabilization of climate forcing at a substantially reduced cost relative to mitigating emissions of CO_2 alone[2,4,68].

These illustrative examples demonstrate the implications of different LLGHG loss timescales for stabilizing and reducing future radiative forcing. But although large cuts in anthropogenic emissions of LLGHGs are clearly needed to stabilize or reduce total direct climate forcing, the exact reductions needed remain somewhat uncertain because natural fluxes of CO_2, CH_4 and N_2O, and a significant fraction of anthropogenic N_2O emissions, are sensitive to climate. Furthermore, some natural and anthropogenic emissions of N_2O and CH_4 could increase in response to increasing atmospheric concentrations of CO_2, although the magnitude of this sensitivity is uncertain[74].

Indirect impacts of N_2O mitigation

Recent studies also suggest that efforts to mitigate some N_2O emissions may have unintended consequences or offsets affecting other GHGs. In many terrestrial and marine ecosystems, nitrogen availability limits carbon uptake despite additions from human activities that more than double the amount of reactive nitrogen annually added by natural processes to the terrestrial biosphere and augment it by ~25% in the marine environment[41,42,52]. These anthropogenic nitrogen additions have led to increased carbon uptake: approximately 10% of oceanic CO_2 uptake is attributable to the atmospheric transport and deposition of anthropogenic nitrogen, and anthropogenic nitrogen deposited in forests may explain a portion of increases in terrestrial carbon uptake[42,52,75]. Model projections of atmospheric CO_2 in 2100 depend substantially on the magnitude of 'CO_2 fertilization', by which increased CO_2 concentrations lead to enhanced carbon uptake by the biosphere[1]. But simple analyses, coupled models considering nutrient availability and new observational data suggest that future CO_2 fertilization could be reduced partly or entirely by nitrogen limitations[76–81]. These results imply that mitigation efforts to reduce anthropogenic nitrogen additions (and associated N_2O emissions) from certain activities (particularly fossil fuel combustion and biomass burning) may have offsets related to reduced carbon uptake and increased atmospheric CO_2. Nitrous oxide mitigation efforts that reduce atmospheric NO_x, however, may also have indirect climate benefits because they could lead to reduced tropospheric ozone and, potentially, a terrestrial biosphere better able to sequester carbon[82]. Although we cannot at present estimate the overall indirect climate impacts of future N_2O mitigation efforts, we do know that the magnitude of a climate offset will depend on existing soil nitrogen burdens, loss rates of anthropogenic nitrogen from soils, rates for nitrogen remineralization in a warmer climate and in the presence of increased CO_2 concentrations, the influence of NO_x-related tropospheric ozone changes on carbon uptake and the adaptability of carbon/nitrogen ratios in organisms to changing nutrient supply ratios[41,52,76,82–87].

The way forward

The considerations described in this Review highlight a number of important principles and scientific needs for managing future climate

forcing. First, because non-CO_2 GHGs at present account for about one-third of total CO_2-eq emissions and 35–45% of total climate forcing from all LLGHGs (range represents direct forcing to the sum of direct and indirect forcing), cuts in their emissions could substantially lessen future climate forcing. Ancillary benefits to mitigating non-CO_2 GHG emissions include reduced costs for climate mitigation relative to CO_2-only approaches, improvements in air and water quality, reduced acid deposition and decreased eutrophication of aquatic ecosystems[2,4,5,8,68].

Second, cuts in emissions of the shorter-lived, non-CO_2 GHGs, primarily CH_4, could cause a rapid decrease in the radiative forcing attributable to these gases. Such a quick response is not possible from cuts in emissions of CO_2 alone. Reducing peak climate forcing and minimizing the time during which it is enhanced could lessen the possibility that the climate irreversibly crosses a tipping point into a new state[67,70]. Although not explicitly considered here owing to their very short lifetimes (<1 yr), other atmospheric constituents such as tropospheric ozone, aerosols and black carbon also affect climate[1,9,22,67,88]. Efforts to reduce their abundances can lead to significant cooling or warming on even shorter timescales than can cuts in CH_4 emissions[67,88], although both long- and short-lived GHGs influence climate for longer periods than suggested by their lifetimes, owing to time lags associated with heat exchange between the ocean and the atmosphere[60].

Third, the potential benefits of cuts in non-CO_2 GHG emissions have limits. If, for example, anthropogenic emissions of all non-CO_2 GHGs considered here had been reduced to zero in 2010 and in subsequent years, the decline in direct radiative forcing between 2010 and 2050 would not be sufficient to completely offset continued CO_2 increases at present rates (~1 W m^{-2} per 40 yr). Because of these limits, the sustained stabilization of future climate forcing from LLGHGs is only possible with substantial decreases in emissions of CO_2.

Fourth, the stabilization of climate forcing will be managed more effectively with scientific advances that enhance our understanding of the sensitivities of natural GHG fluxes to climate change and that improve our ability to quantify both natural and anthropogenic GHG fluxes. With such advances, the overall effectiveness of mitigation efforts could be assessed and optimized over time. Improved scientific capabilities could also increase our ability to reduce GHG emissions and may provide a better understanding of the precise cuts in anthropogenic emissions needed to stabilize climate forcing during this century.

The principles outlined above suggest that a research agenda for managing future radiative forcing would include additional process-based studies to elucidate better the mechanisms, sensitivities and linkages likely to affect future non-CO_2 GHG emissions and improve methods of deriving inventory-based emission estimates that form the basis for treaty compliance, carbon-based trading markets and the initialization of top-down estimation techniques. Such an agenda would also include enhancing observational networks and improving inverse modelling techniques to allow more accurate estimates of regional emissions. The 2007–2010 CH_4 anomaly is an example of how existing trace-gas measurement networks and modelling capabilities are only marginally capable of diagnosing specific causes of a substantial change in the balance of its sources and sinks.

Despite these gaps in our present understanding, it is clear that there are substantial climate benefits to managing reductions in emissions of both CO_2 and non-CO_2 LLGHGs. The benefit and success of controls on both long- and short-lived gases have been demonstrated by the Montreal protocol, which resulted in a rapid and sustained decrease in atmospheric concentrations of ozone-depleting chemicals even though the most abundant were long lived[56,89]. Lifetimes of GHGs are similarly varied, and managing emissions reductions in consideration of these timescales could provide a sustained stabilization of climate forcing earlier and at lower peak values than might otherwise be achieved.

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