

The indirect global warming potential and global temperature change potential due to methane oxidation

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Received 3 July 2009

Accepted for publication 12 October 2009

Published 21 October 2009

Online at stacks.iop.org/ERL/4/044007

Abstract

Methane is the second most important anthropogenic greenhouse gas in the atmosphere next to carbon dioxide. Its global warming potential (GWP) for a time horizon of 100 years is 25, which makes it an attractive target for climate mitigation policies. Although the methane GWP traditionally includes the methane indirect effects on the concentrations of ozone and stratospheric water vapour, it does not take into account the production of carbon dioxide from methane oxidation. We argue here that this CO₂-induced effect should be included for fossil sources of methane, which results in slightly larger GWP values for all time horizons. If the global temperature change potential is used as an alternative climate metric, then the impact of the CO₂-induced effect is proportionally much larger. We also discuss what the correction term should be for methane from anthropogenic biogenic sources.

Keywords: methane, GWP, GTP, carbon dioxide, climate metric, indirect effect

1. Introduction

The concentration of methane (CH₄) has increased from 715 ppbv in pre-industrial times to 1774 ppbv in 2005. The methane lifetime is about 10 years and is largely a function of the global OH concentration in the atmosphere, the reaction with which represents the main sink of methane. The radiative efficiency of methane per unit concentration is relatively large, at least compared to carbon dioxide. Coupled to the significant increase in its concentration, this is why methane is the second most important anthropogenic greenhouse gas in the atmosphere with a radiative forcing (RF) of 0.48 W m⁻² in 2005 relative to pre-industrial conditions (Forster *et al* 2007).

There is an ongoing debate on the most appropriate time for methane emission cuts in the context of multi-gas policies aiming at climate change stabilization (Hansen *et al* 2000, Manne and Richels 2001, van Vuuren *et al* 2006). This issue is intricately related to the choice of a climate metric that provides the evolution in time of the exchange rate between

greenhouse gases in climate policies (IPCC 2009). Despite its shortcomings, the global warming potential (GWP) is a widely used climate metric. In particular the GWP with the time horizon of 100 years is used in the Kyoto Protocol. Shine *et al* (2005) introduced a new climate metric, known as global temperature change potential (GTP), to address some of the issues associated with the GWP and cast climate metrics in a form more appropriate to the context of policies seeking stabilization of temperature change at some point in the future (Shine *et al* 2007). The objective of this letter is to document how these two climate metrics should be modified to account for the oxidation of methane into carbon dioxide.

The absolute global warming potential (AGWP) of a gas is the time-integrated radiative forcing up to a given time horizon due to a pulse emission of 1 kg of the gas under present-day background conditions; it has units of W m⁻² kg⁻¹ year. The GWP of a gas is defined as the ratio of its absolute GWP to that of carbon dioxide. Methane is unusual in that the GWP conventionally factors in the indirect climate effects of

its emissions (Forster *et al* 2007). In particular the GWP of methane includes the positive feedback of methane emissions on the methane lifetime (Prather 1994). It also includes the indirect effects of methane emissions on the concentrations of ozone and stratospheric water vapour. These two effects are accounted for by enhancing the net of the direct and lifetime effects. The enhancement factors are 25% and 5% in Ramaswamy *et al* (2001) resulting in GWP estimates of 62, 23 and 7 for time horizons of 20, 100 and 500 years, respectively. The enhancement factor for stratospheric water vapour has been increased to 15% in Forster *et al* (2007) resulting in larger GWP estimates of 72, 25 and 7.6 for the same three time horizons. Note that some of this increase was also due to slightly smaller values (4% for the time horizon of 100 years) for the AGWP of CO₂ used in Forster *et al* (2007) compared to Ramaswamy *et al* (2001).

The absolute global temperature change potential (AGTP) is defined as the global-mean temperature change realized at a given time horizon from a pulse emission of 1 kg of gas. As for the GWP, the GTP of a gas is defined as the ratio of its absolute GTP to that of CO₂. Fuglestedt *et al* (2009) estimated the GTP of methane to be 57, 12 and 4 for time horizons of 20, 50 and 100 years, respectively, including the same indirect effects as Forster *et al* (2007). Because the GTP is sensitive to how much and how fast the climate responds to a radiative forcing, the values are more uncertain and will vary depending on the specific assumptions being made. Fuglestedt *et al* (2009) adopted the same pulse-response model for temperature change as given by Boucher and Reddy (2008) that is used in this work.

Methane is removed from the atmosphere through soil processes (5% of the total sink), destruction in the stratosphere (7%) and oxidation in the troposphere by OH (88% of the total sink). There are two main end products for the atmospheric sink of methane which are water vapour and carbon dioxide. While the RF due to the production of water vapour (only significant in the stratosphere) is factored in the methane GWP, the RF due to production of carbon dioxide is not. Ramaswamy *et al* (2001) did not include the climate forcing caused by CO₂ produced from the oxidation of CH₄ in their GWP estimates because ‘as discussed in the Second Assessment Report, it is often the case that this CO₂ is included in national carbon production inventories’ and ‘including the CO₂ production from CH₄ could result in double counting this CO₂’. Forster *et al* (2007) did not question this statement. However its origin is unclear and it certainly does not apply for all anthropogenic sources of methane. The 1996 IPCC guidelines (IPCC 1996) specify that reported CO₂ emissions for fuel combustion include C emitted as CH₄. However reported CO₂ emissions for most of the other sectors (e.g. transportation, industrial processes, and fugitive sources from fossil-fuel production) do not include C emitted as CH₄ (Eggleston 2009). In the 2006 IPCC guidelines on emission inventories (IPCC 2006)—not yet adopted by the United Nations Framework Convention on Climate Change—none of the CO₂ emissions include any C emitted as CH₄.

2. Model of the methane impacts

Here we revisit this issue and argue that the methane-induced RF by CO₂ should be included in the methane GWP at least for some methane sources. We make here a simple calculation of the indirect CO₂ effect due to methane sinks.

- Oxidation of CH₄ in the atmosphere is largely dominated by its reaction with OH, with carbon dioxide as the end product and methanol, formaldehyde and carbon monoxide as intermediate products. Because these intermediate products are deposited at the surface, or washed out, not every molecule of methane oxidized in the atmosphere results in a molecule of CO₂. Our calculations with a full chemical transport model STOCHEM (e.g. Collins *et al* 2009) show that, in the troposphere, a change in the CH₄ + OH rate of 1 mol leads to a 0.61 mol change in the CO₂ production. It is likely that a fraction of the intermediate products that are deposited at the surface are re-emitted by soils and oceans as CO₂, but there is little in the literature to assess how large this fraction might be. To account for these uncertainties, we therefore take 50% and 100% as lower and upper bounds of how much of the methane oxidized by OH ends up as CO₂. We are unaware of any other published estimates of the rate of conversion of CH₄ to CO₂.
- In the upper stratosphere, methane is also destroyed by excited oxygen atoms (O(¹D)) with again CO₂ as the end product. Because the potential to be deposited at the surface is much less for intermediate products released in the stratosphere, we consider that all of the methane destroyed in the stratosphere returns to the atmosphere as CO₂.
- The consumption of atmospheric methane by soils occurs through microbial oxidation processes (Ridgwell *et al* 1999). Methanotrophic bacterial populations first oxidize CH₄ into methanol (CH₃OH) which is oxidized further into formaldehyde (HCHO). Formaldehyde can be used to grow bacteria and ends up as organic matter, but part of it will be oxidized into CO₂. Thus the fate of the carbon atoms from the CH₄ oxidized in soils is not clear, but it is likely to be re-emitted as CO₂ on timescales typical of soil carbon residence times. We take 0% and 100% as lower and upper bounds of how much of the methane lost in the soil sink ends up as CO₂.

This gives a lower bound of 0.51 (=0.50 × 88% + 1 × 7% + 0 × 5%) and an upper bound of 1.0 for the fraction of methane that is converted to carbon dioxide. For the upper bound calculation we consider that all the CO₂ is emitted instantaneously after the methane loss, thus neglecting any time lag introduced by the processing of the C by soils and ocean.

We model the CH₄ atmospheric concentration as an exponential decay assuming a 12 year perturbation lifetime which factors in the methane positive feedback on itself (i.e., the lifetime effect), as in Prather *et al* (2001) and Ramaswamy *et al* (2001). We follow Forster *et al* (2007) and enhance the CH₄ direct RF by 40% to account for both the O₃ and

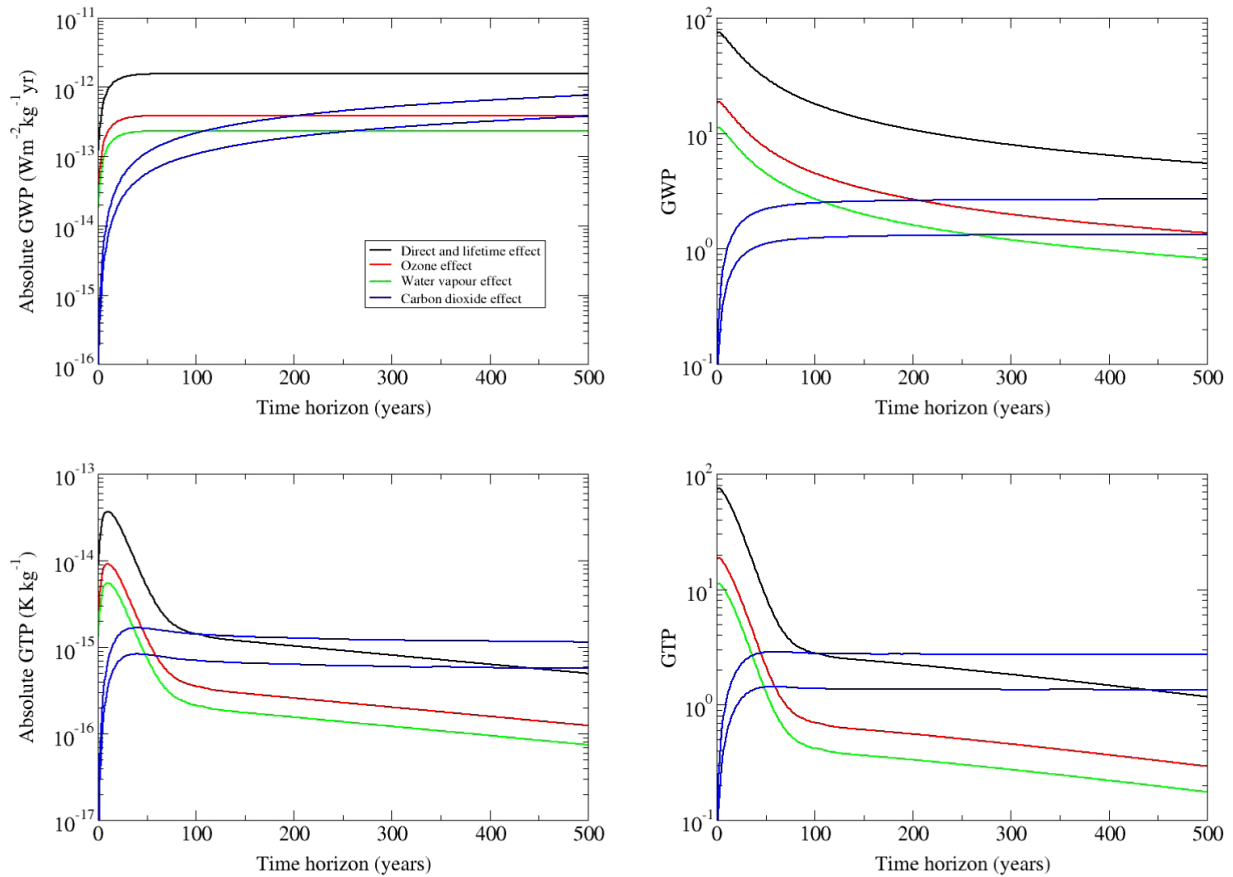


Figure 1. Absolute GWP, absolute GTP, GWP and GTP for methane as a function of the time horizon: direct and lifetime effect (black), indirect O₃ effect (red), indirect H₂O effect (green) and lower and upper bounds of the indirect CO₂ effect for fossil methane (blue).

Table 1. Direct and indirect GWPs and GTPs for methane according to our simple model. Lower and upper bounds are given for the indirect CO₂-induced effect. Note that the GTP values are sensitive to the assumed climate sensitivity parameter used in the model.

Time horizon	Direct and lifetime effect	Indirect O ₃ -induced	Indirect H ₂ O-induced	Indirect CO ₂ -induced fossil source	Indirect CO ₂ -induced anthropogenic biogenic source
GWP 20 years	51.2	12.8	7.7	0.7–1.5	–0.8–0.0
GWP 100 years	18.0	4.5	2.7	1.2–2.5	–1.3–0.0
GWP 500 years	5.5	1.4	0.8	1.3–2.7	–1.4–0.0
GTP 20 years	40.8	10.2	6.1	1.0–1.9	–0.9–0.0
GTP 100 years	2.8	0.7	0.4	1.4–2.8	–1.4–0.0
GTP 500 years	1.2	0.3	0.2	1.4–2.7	–1.3–0.0

stratospheric water vapour effects. A simple enhancement factor is a crude representation of the indirect effect due to stratospheric water vapour because it neglects the time lag between the CH₄ and H₂O radiative forcings, due to the timescale of methane mixing in the stratosphere and the lifetime of stratospheric water vapour. While the timing of the RF does not really matter when calculating a GWP—as long as the time horizon is long enough—this assumption would marginally affect the GTP calculation. We follow the methodology of Boucher and Reddy (2008) to estimate the direct and indirect GWP and GTP. We model the CO₂ concentration using a CO₂ impulse response function and the temperature response using a temperature impulse response function to a unit RF. The details of our calculations are given in the appendix.

3. Results and discussion

The results are displayed in figure 1 and table 1. Our GWP estimates are in perfect agreement with those from Forster *et al* (2007). Our GTP values are also essentially identical to those in Fuglestedt *et al* (2009) who adopted a similar methodology, but calculated the values independently. While the indirect CO₂-induced methane GWP is small for short time horizons, it becomes significant compared to the direct GWP for longer time horizons and it is the dominant term for the GTP for time horizons longer than about 100 years (upper bound) and 400 years (lower bound). The upper bound of the CO₂-induced methane GWP adds about 10% to the net methane GWP for a time horizon of 100 years; this is of comparable magnitude to the increase in the estimates of the methane GWP that occurred between the 2001 and 2007 IPCC assessments. The CO₂-

induced effect adds roughly 50% to the GTP for a time horizon of 100 years. It can easily be shown that the indirect CO₂-induced GWP and GTP for methane both converge towards $44/16 \times \delta$ as the time horizon increases, where δ is the fraction of CH₄ that ends up as CO₂.

The GTP is more sensitive to the inclusion of the CO₂ effect than the GWP because it is a fundamentally different metric. The GWP is a time-integral of the forcing and so retains the memory of the strong, relatively short-lived, direct methane forcing even for long time horizons. The GTP, by contrast, calculates the temperature at a given time after an emission; hence for time horizons long compared to the lifetime of methane, the direct impact of methane on temperature is largely forgotten, while the effects of the much more persistent CO₂ forcing on temperature remain (Shine *et al* 2007).

We address now the implications of our results for the overall uncertainty of the methane GWP and focus on the 100 year time horizon (a discussion of the methane GTP uncertainties is outside the scope of this study). The direct GWP for methane is taken to be $18 \pm 35\%$ (5–95% confidence range, i.e. 2- σ uncertainty from Forster *et al* (2007)). We adopt an ad hoc 1- σ uncertainty of 20% for the indirect effect of methane on ozone production and a 2- σ uncertainty of 70% for the indirect effect of methane on stratospheric water vapour (Forster *et al* 2007). We assume a Gaussian distribution of these errors. The CO₂ indirect GWP is also uncertain but well bounded and we assume a flat distribution of the error between 1.2 and 2.5, which corresponds to a total CH₄-to-CO₂ conversion factor ranging from 0.51 to 1.0, as discussed above. This encompasses both the uncertainties on the conversion rate of CH₄ into CO₂ in the atmosphere and the fate of the CH₄ that is oxidized into soils. We assume here that all these uncertainties are independent to each other and perform a Monte Carlo simulation to estimate an overall uncertainty range for the methane GWP. Under this set of assumptions, the 100 year GWP for fossil-fuel methane is estimated to be 27.1 ± 3.4 and 25.2 ± 3.4 (1- σ uncertainty) with and without the methane oxidation effect, respectively. It is clear that the CO₂ indirect effect shifts the PDF of the methane GWP to larger values but does not substantially increase the uncertainty which is dominated by the uncertainty on the largest components to the GWP.

It should be noted that the above calculations are only valid for methane emission from fossil reservoirs for which the atmospheric oxidation of the CH₄ molecule should be treated as a net source. For anthropogenic biogenic sources, however, the methane release comes from anaerobic decomposition of organic carbon molecules which were formed through photosynthesis in the recent past. From a carbon cycle point of view, the CO₂ molecule initially removed through photosynthesis will return to the atmosphere when the carbon released as the methane molecule is eventually oxidized to CO₂ in the atmosphere. It can be argued that methane emissions from ruminants, crop waste and rice paddies all come from young organic matter so that a molecule of CH₄ would have removed a molecule of CO₂ from the atmosphere. The implication of this is shown in the last column of table 1. If

the lower bound of the CO₂-induced correction is adopted, the discounting of CO₂ results in smaller GWP and GTP values than in Forster *et al* (2007) and Fuglestedt *et al* (2009). If the upper bound is adopted instead, then the removal of one molecule of CO₂ is exactly compensated by the addition of one molecule of CO₂ from the methane sink. In that case the GWP and GTP values of Forster *et al* (2007) and Fuglestedt *et al* (2009) are appropriate for anthropogenic biogenic CH₄. Methane emissions from biomass burning, wetlands and landfills would correspond to carbon with a range of ages so that only a fraction of the CO₂ should be discounted.

4. Conclusions

In conclusion we recommend somewhat larger values for the methane GWP than suggested by Forster *et al* (2007) when the methane comes from fossil sources. The revised rounded value for the 100 year GWP would be 27 if we discard the methane oxidation products that are scavenged into soils (lower bound) and 28 if one considers that every molecule of CH₄ ends up as CO₂ (upper bound). For anthropogenic biogenic sources we recommend the discounting of CO₂ that has been taken out of the atmosphere in the first place, which results in a 100 year GWP either lower by 1.0 (if one assumes that only a fraction of the methane molecules end up as CO₂) or equal (if one assumes that all methane molecules are oxidized to CO₂) to the current estimate. Accounting for the CO₂-induced indirect effect of methane emissions has an even larger relative impact should the GTP be used as a metric instead of the GWP. For GTP-100 years and longer time horizons, our upper bound for the indirect CO₂ correction is larger than the direct CH₄ effect.

Additional effects, not considered here, may also play a role, such as the fact that the ozone produced by the methane could cause plant damage, and hence influence the carbon cycle, or the influence of the methane-induced changes in OH on other climatically important constituents. Work is ongoing to quantify these additional effects.

Acknowledgments

This work was supported by the Joint DECC and Defra Integrated Climate Programme—DECC/Defra (GA01101). KPS acknowledges support from the European Commission FP6 Integrated Project, QUANTIFY. OB would like to thank Simon Eggleston for useful discussion. The reviewers are thanked for their helpful comments.

Appendix

We use analytical impulse response functions (IRF) to model GWPs and GTPs, already described in Boucher and Reddy (2008). The CH₄ IRF is a simple exponential decay

$$[\text{CH}_4](t) = [\text{CH}_4](t_0) + E_{\text{CH}_4} e^{-(t-t_0)/\tau}$$

where E_{CH_4} is the emission at time t_0 (expressed in volume mixing ratio) and τ is the CH₄ perturbation lifetime (12 years). A fraction, α , of the oxidized CH₄ ends up as CO₂, which gives a CO₂ emission rate

$$E_{\text{CO}_2}(t) = \alpha E_{\text{CH}_4} \tau^{-1} e^{-(t-t_0)/\tau}.$$

Table A.1. Parameters of the impulse response functions used in this study.

	$i = 0$	$i = 1$	$i = 2$	$i = 3$
a_i (unitless)	0.217	0.259	0.338	0.186
b_i (years)		172.9	18.51	1.186
c_i (K (W m ⁻²) ⁻¹)		0.631	0.429	
d_i (years)		8.4	409.5	

The CO₂ IRF relies on a pulse experiment from the Bern model (updated from Joos and Bruno 1996). The fraction of carbon emitted at time $t = 0$ which is left in the atmosphere at time t is expressed as

$$f(t) = a_0 + \sum_i a_i \exp(-t/b_i)$$

with $\sum_i a_i = 1$ by construction (table A.1). The CO₂ atmospheric concentration at time t_1 from an emission profile $e(t)$ can then be approximated as a convolution of $e(t)$ with $f(t)$

$$[\text{CO}_2](t_1) = [\text{CO}_2](t_0) + \int_{t_0}^{t_1} e(t) f(t_1 - t) dt.$$

The emission profile $e(t)$ is taken to be a pulse emission for the calculation of the CO₂ GWP and GTP or $E_{\text{CO}_2}(t)$ defined above when calculating the CO₂-induced indirect methane GWP and GTP. We follow Ramaswamy et al (2001) to calculate the radiative forcing (RF) as a function of the atmospheric concentrations of CO₂ and CH₄. Baseline concentration values for CO₂, CH₄ and N₂O are those for 2005. Moreover the direct RF by CH₄ is increased by 40% to account for the O₃ and stratospheric water vapour effect, as in Forster et al (2007). The absolute GWP for CO₂ or CH₄ at a time horizon T is then calculated as $\text{AGWP}(T) = \int_{t_0}^{t_0+T} \text{RF}(t) dt$ using a pulse emission of 1 kg.

The climate response (in terms of global surface temperature change) is estimated from an impulse response function to RF (see Boucher and Reddy (2008) for more details):

$$\delta T(t) = \sum_i c_i/d_i \exp(-t/d_i)$$

with the c_i and d_i coefficients given in table A.1. The climate responds with a short timescale d_1 and a longer timescale d_2 . The equilibrium climate sensitivity, as the sum of the c_i coefficients, is 1.06 K (W m⁻²)⁻¹ or 3.9 K for a doubling of the CO₂ concentration. The impulse response function for surface temperature has been derived from more than 1000 simulated years of an experiment with the HadCM3 climate model in which atmospheric CO₂ concentrations were quickly ramped up to four times the pre-industrial levels before being held constant. We believe that the experimental setup favouring the longer timescales of the climate response is responsible for the slightly larger climate sensitivity than reported elsewhere for the HadCM3 model. The climate response IRF can then be used to estimate the global surface temperature change at time t_1 from a RF profile $\text{RF}(t)$ as

$$\Delta T(t_1) = \int_{t_0}^{t_1} \text{RF}(t) \delta T(t_1 - t) dt.$$

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