Int J Life Cycle Assess (2016) 21:1069–1075
DOI 10.1007/s11367-016-1091-z

CARBON FOOTPRINTING

Methane oxidation, biogenic carbon, and the IPCC's emission metrics. Proposal for a consistent greenhouse-gas accounting

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Received: 10 July 2015 / Accepted: 9 March 2016 / Published online: 22 March 2016

Abstract
Purpose The fifth assessment report by the IPCC includes methane oxidation as an additional indirect effect in the global warming potential (GWP) and global temperature potential (GTP) values for methane. An analysis of the figures provided by the IPCC reveals they lead to different outcomes measured in CO_2-eq., depending on whether or not biogenic CO_2 emissions are considered neutral. In this article, we discuss this inconsistency and propose a correction.
Methods We propose a simple framework to account for methane oxidation in GWP and GTP in a way that is independent on the accounting rules for biogenic carbon. An equation with three components is provided to calculate metric values, and its application is tested, together with the original IPCC figures, in a hypothetical example focusing on GWP100.
Results and discussion The hypothetical example shows that the only set of GWP100 values consistently leading to the same outcome, regardless of how we account for biogenic carbon, is the one proposed in this article. Using the methane GWP100 values from the IPCC report results in conflicting net GHG emissions, thus pointing to an inconsistency.
Conclusions In order to consistently discriminate between biogenic and fossil methane sources, a difference of 2.75 kg CO_2-eq. is needed, which corresponds to the ratio of the molecular weights of CO_2 and methane (44/16). We propose to correct the GWP and GTP values for methane accordingly.

Keywords Biogenic carbon · Carbon footprinting · Global temperature change potential · Global warming potential · Life cycle assessment · Methane

1 Introduction

The global warming potential (GWP) was presented in the First IPCC Assessment report (Houghton et al. 1990) as a metric for transferring emissions of different greenhouse gasses (GHG) to a common scale. In particular, the GWP for a time horizon of 100 years (GWP100) was later adopted as metric to implement the multi-gas approach embedded in the United Nations Framework Convention on Climate Change and made operational in the 1997 Kyoto Protocol. Despite its serious limitations (see Shine 2009), the GWP100 remains to this date the most popular metric to assess GHG emissions, not only in the context of national GHG inventories but also in life cycle assessment (LCA) and carbon footprinting.

In 2013, the IPCC released its fifth assessment report (IPCC 2013), which includes updated values for GWP. In table 8.A.1 of this report (Myhre et al. 2013, p. 731), the updated GWP values are shown for common GHG in different time horizons, together with those for the alternative metric global temperature change potential (GTP) (Shine et al. 2005). A new feature in the GWP and GTP values for methane is that they include an additional indirect effect, namely that from the oxidation of

Responsible editor: Hans-Jürgen Garvens

Electronic supplementary material The online version of this article (doi:10.1007/s11367-016-1091-z) contains supplementary material, which is available to authorized users.

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methane to CO_2. This effect is captured to reflect the fact that methane will eventually break down to CO_2 in the atmosphere, and this CO_2 constitutes an additional burden to be attributed to the parent molecule, thus increasing the overall impact of a methane emission. The new IPCC report attributes a GWP100 of 28 kg CO_2-eq. per kg methane from biogenic sources and of 30 kg CO_2-eq. per kg methane from fossil sources (Table 1). In this way, the IPCC discriminates between biogenic and fossil methane, where the difference of 2 kg CO_2-eq. attributed to fossil methane is ascribed to the contribution from oxidation to CO_2. This difference of 2 kg CO_2-eq. is based on Boucher et al. (2009), who assessed the contribution of methane oxidation to GWP as well as to GTP.

The practice of discriminating GHG emissions depending on the carbon origin is not new. It is common to assume that CO_2 originating from biomass has no net contribution to global warming, and although it is reported in GHG inventories, it is usually assigned a GWP of zero. As the IPCC states: "carbon dioxide from the combustion or decay of short-lived biogenic material removed from where it was grown is reported as zero" and "…it is assumed that the [CO_2] emission is balanced by carbon uptake prior to harvest" (Rypdal et al. 2006). Nevertheless, in reality, there is no chemical distinction between carbon from biogenic and fossil sources, so one could argue that releasing 1 kg of CO_2 has an impact regardless of the carbon origin. In line with this thinking, the ILCD handbook on life cycle assessment (European Commission 2010, p. 226) advocates for an equal treatment of CO_2 emissions, regardless of their origin. The same applies to other guidelines and standards such as the GHG Protocol (WRI 2011, p. 89) and ISO/TS 14067 (ISO 2013). In this way, an emission of 1 kg CO_2 would be attributed a GWP of 1 kg CO_2-eq., whereas uptake of 1 kg CO_2 from the atmosphere must be balanced with a GWP of −1 kg CO_2-eq. This is particularly important when the temporal delays between emissions and uptake are long enough to influence the atmospheric concentration of CO_2, and also when not all uptake is emitted, e.g., when some biogenic materials are stabilized in landfills.

Once it is decided to distinguish between biogenic or fossil carbon, this does not only affect CO_2 uptake and release. It also has implications on other carbon sources and sinks, in particular, on how we account for long-term carbon storage and methane emissions. Christensen et al. (2009) reviewed different accounting methods for CO_2 emissions when calculating carbon footprints of solid waste treatment. One of their conclusions was that when biogenic CO_2 emissions are assumed neutral (GWP = 0), a consistent accounting requires long-term biogenic carbon storage in sinks like landfills, soil, etc., to be assigned a GWP of −1 kg CO_2-eq. per kg CO_2 that is stored beyond the chosen time horizon. On the other hand, when all carbon is treated as equal, this negative GWP is not required. A summary of these CO_2 accounting rules is displayed in Table 2. Concerning methane, the reasoning behind discriminating biogenic from fossil sources lies in the fact that in the case of a biogenic methane emission, the CO_2 produced by methane oxidation is balanced by the CO_2 uptake when the biomass containing the carbon for this methane release was originally formed. However, if we decided to treat all carbon as equal, a single GWP100 value would be required, namely that for fossil methane, which would be applied regardless of the carbon origin.

Table 1 GWP and GTP values for methane from fossil and biogenic sources in different time horizons, in kg CO_2-eq/kg methane, according to the IPCC 5th Assessment report (Myhre et al. 2013, p. 731)

Methane source	GWP		GTP		
	20 years	100 years	20 years	50 years	100 years
CH_4 biogenic	84	28	67	14	4
CH_4 fossil	85	30	68	15	6

The first method accounting for the contribution of chemical oxidation in the atmosphere was the life cycle impact assessment method EDIP97 (Hauschild and Wenzel 1998), which provided characterization factors for all volatile organic compounds of fossil origin. More recently, the need to account for methane oxidation when assessing GHG emissions has been addressed by other authors (Boucher et al. 2009; Muñoz et al. 2013), and the inclusion of this aspect in the new IPCC report can only be considered as a positive development. However, after a careful analysis of these new figures for biogenic and fossil methane, we argue that they are inconsistent. By inconsistent, we mean that their application will lead to different outcomes, measured in CO_2-eq., depending on the carbon accounting rules considered by the practitioner. In this article, we describe this inconsistency, focusing on GWP100, and we propose a correction for both GWP and GTP. We then apply these corrected values in a hypothetical example to test their consistency.

Table 2 Two sets of consistent GWP and GTP values for CO_2 in kg CO_2-eq/kg. Based on Christensen et al. (2009)

CO_2 sources and sinks	Approach 1: Biogenic CO_2neutral	Approach 2: Biogenic CO_2not neutral
CO_2uptake	0	−1
CO_2 biogenic, emitted	0	1
CO_2 fossil, emitted	1	1
CO_2 biogenic, long-term storage	−1	0
CO_2 fossil, long-term storage	0	0

2 Methods

2.1 A proposal for consistent metric values for biogenic and fossil methane

In order to differentiate the GWP and GTP of methane from biogenic and fossil sources, we can define the metric as constituted by three components, as shown in Eq.(1):

$$\text{Metric}_{TH} = \text{Pulse} + \text{Oxidation} - \text{Biogenic correction} \quad (1)$$

where Metric_{TH} is the GWP or GTP of methane in a given time horizon, Pulse is the metric value related to the pulse emission of 1 kg methane, Oxidation is the metric value related to the breakdown of methane into CO_2, and Biogenic correction is the metric value related to the recent CO_2 uptake by biomass through photosynthesis (all in kg CO_2-eq./kg methane).

The *Pulse* component in Eq. (1) is directly obtained from the IPCC report. For instance, it takes the value of 28 kg CO_2-eq./kg methane (table 8.A.1 in Myhre et al. 2013, p. 731) for GWP100.

As for *Oxidation*, the amount of CO_2 formed by complete oxidation of methane is dictated by stoichiometry, where 1 kmol methane, weighting 16 kg/kmol breaks down into 1 kmol CO_2, weighting 44 kg/kmol, thus 1 kg methane breaks down into 44/16 = 2.75 kg CO_2. However, the GWP100 of this release is lower in CO_2-eq., given that this CO_2 is not released in year zero, but slowly released as methane decays. If this delay is taken into account assuming that a molecule of CO_2 is instantaneously formed when a molecule of methane disappears, then *Oxidation* corresponds to approximately 2.5 kg CO_2-eq./kg methane. *Oxidation* values decrease with shorter time horizons and increases with longer time horizons up to a limit of 2.75. As examples, in the ESM 1: supplementary material, we have calculated GTP and GWP values for *Oxidation* for the three time horizons considered in the IPCC report: 20, 50, and 100 years.

Since the biological CO_2 uptake and the subsequent release as methane are assumed to occur in a short time frame, *Biogenic correction* equals 2.75 kg CO_2-eq./kg methane. Obviously, *Biogenic correction* only applies to methane from biogenic sources, whereas for fossil methane, this factor is zero. Similarly, in case there is no need to discriminate carbon origin, *Biogenic correction* also takes a value of zero, whereby $Metric_{TH}$ for fossil and biogenic methane are the same and take the value for fossil methane.

It can be seen that *Biogenic correction* (2.75) has a higher value than *Oxidation* (2.5) in GWP100. The reason is that while CO_2 uptake is assumed to take place in year zero, its release due to methane oxidation is a slower process. One hundred years after a methane pulse is emitted, only approximately 90 % of the carbon is oxidized to CO_2, leading to the *Oxidation* value of 2.5. The remaining 0.25 kg CO_2 needed to close the balance of CO_2 uptake and release are "stored" in the methane molecule and therefore not counted as an emission when a 100-year time horizon is chosen.

We can apply Eq. (1) to GWP 100 as follows:

- GWP100 = 28 + 2.50 - 2.75 = 27.75 kg CO_2-eq./kg methane from biogenic sources
- GWP100 = 28 + 2.50 = 30.50 kg CO_2-eq./kg methane from fossil sources

It can be seen that the net difference between the two values is 2.75 kg CO_2-eq.

Based on Eq. (1), we can calculate the GWP and GTP values for methane in different time horizons, as shown in Table 3. In the following section, we test the GWP100 values for consistency, along with those provided in table 8.A.1 in the IPCC report.

2.2 Consistency test

In order to test Eq. (1) for consistency, we apply it in the calculation of GWP100 values and then apply the obtained values in a GHG emission calculation example as described in (Muñoz et al. 2013, appendix), where it is assumed that a product incorporating 2 kg carbon (1 kg from biogenic origin and 1 kg from fossil origin) is deposited in a landfill. Fifty percent of the carbon degrades to CO_2 and methane, and the remaining 50 % stays stored in the landfill. The mass balance for this example is shown in the middle column of Table 4.

We assess GHG emissions in CO_2-eq. for this example, based on the following sets of GWP100 values for methane:

- Those from Table 3, based on Eq. (1), i.e., the approach proposed in this article.
- Those provided in table 8.A.1 in Myhre et al. (2013, p. 731).

We test these two sets of GWP100 values according to the two mentioned carbon accounting approaches:

1. We do not discriminate GWP100. Biogenic and fossil carbon sources are treated equally.
2. We discriminate GWP100 according to the carbon source (biogenic/fossil), where biogenic CO_2 emissions are considered neutral.

3 Results

The results of our consistency test are shown in Table 5, which shows in its upper half the GWP100 values applied, and in the lower half, the result of applying them

Table 3 Proposed set of consistent GWP and GTP values for methane from fossil and biogenic sources in different time horizons, in kg CO_2-eq/kg methane, calculated with Eq. (1). See the Electronic Supplementary Material for details

Methane source	GWP		GTP		
	20 years	100 years	20 years	50 years	100 years
CH_4 biogenic:					
Pulse	84.00	28.00	67.00	14.00	4.00
Oxidation	1.40	2.50	1.90	2.80	2.80
Biogenic correction	−2.75	−2.75	−2.75	−2.75	−2.75
Net	82.65	27.75	66.15	14.05	4.05
CH_4 fossil:					
Pulse	84.00	28.00	67.00	14.00	4.00
Oxidation	1.40	2.50	1.90	2.80	2.80
Biogenic correction	0	0	0	0	0
Net	85.40	30.50	68.90	16.80	6.80

to the exchanges from our hypothetical product disposal shown in Table 4. The bottom line in Table 5 shows the net GHG emissions, in CO_2-eq.

We consider a set of GHG metric values as consistent only if they lead to the same CO_2-eq. outcome, regardless of whether the practitioner chooses carbon accounting approach 1 or 2 as defined in section 2.2. As it can be seen in Table 5, the only set of GWP100 values consistently leading to the same outcome, regardless of how we account for biogenic carbon, is the one proposed in this article, where the GWP100 for methane is based on Eq. (1). Using the methane GWP100 values from the IPCC report (Myhre et al. 2013, p. 731), results in conflicting net GHG emissions, thus pointing to an inconsistency. In the ESM 1: supplementary material, we show how we arrive to the same conclusion when we apply GWP20 as well as GTP20, GTP50, and GTP100.

Table 4 Mass balance for a hypothetical product disposed of in a landfill (Muñoz et al. 2013, appendix)

MASS BALANCE	As kg carbon	As kg CO_2 or CH_4
Input		
CO_2 fossil	1	3.67
CO_2 biogenic	1	3.67
Output		
Emissions:		
CO_2 biogenic	0.25	0.92
CH_4 biogenic	0.25	0.33
CO_2 fossil	0.25	0.92
CH_4 fossil	0.25	0.33
Long-term storage:		
CO_2biogenic	0.5	1.83
CO_2 fossil	0.5	1.83

4 Discussion

4.1 The key to consistency in biogenic vs. fossil methane metric values

The reason why our proposed GWP100 values are the only ones achieving consistency when applied in practice, is the fact that when we discriminate the carbon source, the metric values for biogenic and fossil methane show a difference of 2.75 kg CO_2, i.e., the value attributed to *Biogenic correction* in Eq. (1). This 2.75 factor is universally valid, in the sense that it is neither GWP-specific nor time horizon-specific; regardless of whether we choose GWP or GTP in any given time horizon, this difference of 2.75 must be kept, in order to balance the amounts of carbon exchanged as CO_2 and methane. Therefore, in future updates of the GWP and GTP metrics by the IPCC a consistent accounting of biogenic vs. fossil methane would allow for changes in the absolute metric values, but not in the difference between them, which would need to be kept at 2.75 kg CO_2/kg methane, instead of 2 kg CO_2/kg methane as currently displayed in the IPCC report.

4.2 The GWP values for methane in the IPCC report

The inconsistency identified for the GWP values in (Myhre et al. 2013, p. 731) is explained by analyzing its source, namely, the study by Boucher et al. (2009), who assessed the contribution of methane oxidation to GWP as well as to GTP in two scenarios or bounds: the lower bound assumed that 51 % of the carbon in methane is oxidized to CO_2, whereas the upper bound assumed full oxidation to CO_2. Based on these two bounds, GWP and GTP values were calculated for biogenic and fossil methane considering several time

Table 5 Calculation of GWP100 (in kg CO_2-eq.) for the example presented in Table 4

Sets of GWP values	Proposed in this article (Eq. (1), Table 3)		IPCC report (Myhre et al. 2013, p. 731)	
	Approach 1: Biogenic CO_2 not neutral	Approach 2: Biogenic CO_2 neutral	Approach 1: Biogenic CO_2 not neutral	Approach 2: Biogenic CO_2 neutral
GWP (kg CO_2-eq./kg)				
CO_2uptake	−1	0	−1	0
CO_2 biogenic, emitted	1	0	1	0
CO_2 fossil, emitted	1	1	1	1
CH_4 biogenic, emitted	30.50	27.75	30	28
CH_4 fossil, emitted	30.50	30.50	30	30
CO_2 biogenic, long-term storage	0	−1	0	−1
CO_2 fossil, long-term storage	0	0	0	0
GWP × Exchanges as in Table 4 (kg CO_2-eq.)				
CO_2uptake	−3.67	0.00	−3.67	0.00
CO_2 biogenic, emitted	0.92	0.00	0.92	0.00
CO_2 fossil, emitted	0.92	0.92	0.92	0.92
CH_4 biogenic, emitted	10.17	9.25	10.00	9.33
CH_4 fossil, emitted	10.17	10.17	10.00	10.00
CO_2 biogenic, long-term storage	0.00	−1.83	0.00	−1.83
CO_2 fossil, long-term storage	0.00	0.00	0.00	0.00
Net GHG emissions	18.50	18.50	18.17	18.50

horizons. An interesting finding, with respect to our critique, is that according to Table 1 in Boucher et al. (2009), the difference between fossil and biogenic methane, for GWP100, is:

- Lower bound: 26.4–23.9 = 2.5
- Upper bound: 27.7–25.2 = 2.5

As it can be seen, according to Boucher et al. (2009), the GWP100 for fossil methane should not be 2 but 2.5 kg CO_2-eq. higher than the one for biogenic methane, regardless of the assumptions. Thus, table 8.A.1 in the IPCC report does not properly reflect the results from Boucher et al. (2009). If we look at the precise GWP100 values for biogenic and fossil methane in the IPCC report, these are 28.49 and 29.73, whereby a net difference of 1.24 appears. This difference then appears as 2 when looking at the GWP100 rounded with no decimals. The value of 1.24 is due to an error when implementing the lower bound results from Boucher et al. (2009) in the IPCC report table (William Collins, U. of Reading, personal communication). Nevertheless, regardless of whether the lower or higher bound from Boucher et al. (2009) is chosen, we see that the net difference between biogenic and fossil methane is 2.5 and not 2.75 as proposed in this article. Although the calculations are not shown in this article, it can easily be demonstrated that using a net difference of 2.5 equally leads to inconsistent results, although the error, i.e., the difference between the results obtained by approaches 1 and 2 is of lower magnitude than when the values in the IPCC report are used. This is because the 2.5 difference factor is closer to 2.75 than the difference factor of 2 used in the IPCC report.

4.3 Uncertainty

One of the assumptions made in our calculations is that CO_2 uptake by biomass and release of this carbon as methane happens in the same year. This is a simplification, since harvested biomass might be stored for some time, with forestry systems being the clearest example, due to their relatively long rotation times compared to crops. If the carbon is released in the atmosphere as CO_2 before an equal amount is recaptured in regrowing biomass, this CO_2 contributes to global warming (Cherubini et al. 2011). These cases require a dynamic approach to accounting of biogenic carbon flows (Levasseur et al. 2010; Cherubini et al. 2011). Therefore, our *Biogenic correction* factor is only a good representation for methane releases when there is no or little delay between carbon uptake and release.

More importantly, it must be highlighted that the calculation of GWP (the Pulse component in Eq. (1)) is subject to substantial uncertainties. For methane, the IPCC estimated an uncertainty of ±30 and ±40 % for GWP100 and GWP20, respectively (for 5 to 95 % uncertainty range), taking into account uncertainties related to radiative efficiencies,

perturbation lifetimes, indirect effects, and in the absolute GWP for the reference gas CO_2 (Myhre et al. 2013, p. 713). Therefore, the corrections we propose in this article could be seen as small enough to be considered as insignificant. However, when assessing the uncertainty of our calculated GWP values, this should be done by considering the respective uncertainty of the different components in Eq. (1). The *Pulse* component in Eq. (1) is 28 kg CO_2-eq./kg $CH_4 \pm 30$ %, thus having a relatively high uncertainty. The *Oxidation* component is 2.5 for a time horizon of 100 years and has a relatively lower uncertainty, mainly driven by the time-dependent decay of CO_2 in the atmosphere. According to Joos et al. (2013), the time-integrated uncertainty for this decay is ±15 and ±25 % (5 to 95 % uncertainty range) for GWP20 and GWP100, respectively. At the same time, 1 kg of methane necessarily originates from 2.75 kg CO_2 absorbed by growing biomass. This relationship is driven by basic stoichiometry and therefore the *Biogenic correction* factor in Eq. (1) has no uncertainty. Overall, we admit that proposing, e.g., a GWP100 of 27.75 kg CO_2-eq./kg biogenic methane gives a false impression of precision; however, this precision is required for consistency, as shown in our simple example. This figure could be rounded if desired to 28, but then, as we have seen, in order to be consistent we would have to use a GWP100 for fossil methane of 30.75 kg CO_2-eq./kg fossil methane (28 + 2.75), and this figure cannot be rounded to 31. We could see this if for example in Table 5 we used 28 and 30.75 as values for biogenic and fossil methane, respectively. In such a case, the results of approach 1 and 2 would be consistent (18.67 in both), while if we used 28 and 31 instead the results would be inconsistent (18.83 in approach 1, 18.75 in approach 2).

4.4 Implications for GHG accounting

From the two GHG accounting approaches described in this article, i.e., treating all carbon sources as equal in terms of climate change impacts vs. discriminating the impact of emissions from biogenic and fossil carbon sources, it seems that the first one is gaining more acceptance (as shown in several standards and guidelines cited in the introduction), but still the second one is commonly applied by LCA practitioners. If we are to discriminate the impact of CO_2 and methane emissions according to biogenic or fossil sources, it is important that this is done consistently to avoid unnecessary errors, even if these are of a small magnitude. Methane is the second most important GHG globally, and it is also the main driver in the carbon footprint of certain products and services, such as solid waste landfilling, palm oil production, and beef and milk production. The corrections proposed in this article are not expected to significantly affect the GHG profiles of these activities, but they contribute to bringing more clarity and better alignment of methods in one of the areas that receives most attention in environmental assessment.

We think this approach is also relevant for LCA software providers, who very often bear the responsibility of deciding what characterization factors assign to biogenic and fossil carbon emissions in the impact assessment methods that their software provides and which many users around the world will apply. As a matter of fact, this is precisely how the idea of writing this article arose, namely by discussing with a major LCA software provider on how to implement the new IPCC values for GWP.

5 Conclusions

The fifth assessment report by the IPCC for the first time introduced oxidation to CO_2 as an indirect effect to be added to the GWP and GTP of methane. An analysis of the figures provided by the IPCC shows that they are inconsistent, in the sense that their application leads to different CO_2-eq. outcomes, depending on the carbon accounting rules considered by the practitioner. We have proposed a simple framework to properly account for this indirect effect in GHG assessments, which is applicable to both GWP and GTP metrics, in any time horizon. The key conclusion to be highlighted is that in the context of quantifying GHG emissions the only way to consistently discriminating between biogenic and fossil methane sources is by keeping the metric values apart by a difference of 2.75 kg CO_2-eq., which corresponds to the ratio of the molecular weights of CO_2 and methane (44/16).

Acknowledgments The author thanks the useful input received from Dr. Olivier Boucher, CNRS Research Director, and Dr. William Collins, Professor of Atmospheric Chemistry and Earth System Modeling, University of Reading.

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