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# Comparing the heat of combustion of fossil fuels to the heat accumulated by their lifecycle greenhouse gases



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Fossil fuels are the dominant source of primary energy in mod-

ern economies. For example, in the United States (US) in 2011, 36%

of primary energy was supplied by petroleum, 26% by natural gas,

and 20% by coal [1]. Globally in 2010, 32% of primary energy was

supplied by petroleum, 27% by coal, and 21% by natural gas [2].

Fossil fuels are widely used because they provide a convenient,

storable, transportable, and energy-dense form of chemical energy.

This chemical energy can readily be converted to thermal energy

through combustion of the fuels. The heat of combustion can be

used directly to provide such energy services as industrial or resi-

dential heating, or it can in turn be converted to mechanical or

formed and are released into the environment. An important

GHG is carbon dioxide (CO<sub>2</sub>), but significant emissions of methane

(CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) may also occur depending on com-

bustion conditions. These GHGs mix uniformly throughout the

When a fossil fuel is combusted, greenhouse gases (GHGs) are

electrical energy to provide other useful energy services.

## HIGHLIGHTS

• We compare the heat released by fossil fuel combustion to the heat accumulated by their GHGs.

• The direct heat from combustion is minor in relation to the indirect heat accumulated by radiative forcing.

• Fuel cycle emissions contribute significantly to total lifecycle GHG emissions and radiative forcing.

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### 1. Introduction

# ABSTRACT

We compare the heat released directly due to combustion of fossil fuels to the heat accumulated indirectly in the earth system due to the effect of greenhouse gases (GHGs) associated with the fuels. We differentiate between GHG emissions from the combustion products of fossil fuels and from the fuel cycle activities of extracting, processing, and transporting the fuels. We find that the direct release of heat from the combustion of fossil fuels is minor in relation to the indirect accumulation of heat due to radiative forcing. The quantity of indirect heat accumulated by GHGs continues to increase over time, as additional energy is accumulated in the earth system as long as the GHGs remain in the atmosphere. Fuel cycle emissions contribute significantly to total lifecycle GHG emissions and radiative forcing.

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atmosphere and begin to trap heat through the process of radiative forcing. Radiative forcing is an imbalance in the earth system between incoming and outgoing radiation. GHGs allow shortwave light radiation to enter the earth's atmosphere but restrict the exit of longwave heat radiation, resulting in an accumulation of energy within the earth system. The large-scale combustion of fossil fuels currently observed results in significant GHG emissions, raising concern about climate destabilization and consequent impacts to physical, biological, and social systems [3].

In addition to the GHGs emitted directly as combustion products, additional GHGs are emitted from other sources during the full fuel cycle of fossil fuels. Energy is used for creating and operating coal mines and oil and natural gas wells, leading to indirect GHG emissions. In addition,  $CH_4$  is typically emitted from coal mines and from leaks from gas production and transport facilities. Furthermore, process emissions of  $CO_2$  and  $CH_4$  are typically produced at oil refineries. These emissions, which are distinct from the direct emissions from fossil fuel combustion, nevertheless contribute to radiative forcing and must be accounted for in a holistic analysis.

In this contribution we explore whether the heat released directly into the earth system due to combustion of fossil fuels is significant relative to the heat accumulated indirectly in the earth

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system due to the effect of GHGs. Furthermore, we investigate the relative contributions of GHG emissions from the combustion products of fossil fuels and from the fuel cycle activities of extracting, processing, and transporting the fuels.

#### 2. Methods

In this analysis we first estimate the combustion emissions and fuel cycle emissions of  $CO_2$ ,  $N_2O$ , and  $CH_4$  resulting from coal, oil, and natural gas corresponding to 1 J of combustion heat. We then use simple climate models to estimate the energy accumulated in the earth system by the emitted GHGs, based on the gases' radiative efficiency and atmospheric residence time. Finally, we calculate the ratio of heat accumulated by GHGs to heat released by combustion.

Combustion emissions of CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub> are based on default values recommended by IPCC [4]. Emission factors for bituminous coal and natural gas refer to stationary combustion in energy industries, while emission factors for diesel oil refer to mobile combustion in on-road vehicles. These factors are shown in Table 1. As our goal is to compare total heat inputs to the earth system, the direct combustion heat energy of the fossil fuels is in terms of the higher heating value (HHV; gross calorific value) of the fuels, i.e. including the latent heat of vaporization of water produced by the combustion. We adjust values of lower heating value (LHV) obtained from literature to HHV, based on IPCC guidelines [4].

Fuel cycle GHG emissions result from the extraction, processing, and transportation of fuels. Coal emission factors analyzed here are based on US underground bituminous coal mining, and result from energy used for commissioning and operating the mine, mine methane emissions, and transport by train for 940 km [5]. Oil emission factors are based on US diesel fuel production, and result from energy used for commissioning and operating oil wells, transport of crude oil and refined fuel by ship and pipeline, and energy use and emissions from petroleum refining [6]. Transport modes and distances represent actual sourcing of US petroleum refining. Allocation of emissions from crude oil production and transport among the diverse refinery products is done on the basis of volume. Natural gas emission factors are based on US conventional onshore gas production, and result from energy used for commissioning and operating gas wells and transport infrastructure, pipeline transport for 1450 km, and methane leakage from production and transport facilities [7]. These emission factors are summarized in Table 1.

Temporally explicit estimates of radiative forcing resulting from GHG emissions are then made using the simple climate models described by Zetterberg [8], with updated parameter values from IPCC [3,9,10]. The combustion and fuel cycle emissions of  $CO_2$ ,  $N_2O$  and  $CH_4$  are treated as pulse emissions. The atmospheric decay of each pulse emission is estimated using the following equations, which describe the removal of gases from the atmosphere by natural processes at time rates that vary with the GHG [3,9,10]:

Table 1

Combustion and fuel cycle emission factors for bituminous coal, diesel oil, and natural gas (g GHG emitted per J higher heating value). *Source*: [4–7]; adjusted from LHV to HHV.

	Bituminous coal	Diesel oil	Natural gas								
Combustion emissions											
$CO_2$	$9.18 \times 10^{-5}$	$7.06  imes 10^{-5}$	$5.34 imes10^{-5}$								
$N_2O$	$1.43  imes 10^{-9}$	$3.71\times10^{-9}$	$9.52\times10^{-11}$								
CH <sub>4</sub>	$9.52\times10^{-10}$	$3.71\times10^{-9}$	$9.52\times10^{-10}$								
Fuel cycle emissions											
$CO_2$	$1.61  imes 10^{-6}$	$1.43\times10^{-5}$	$4.42\times 10^{-6}$								
$N_2O$	$7.72  imes 10^{-12}$	$2.76\times10^{-10}$	$4.62\times10^{-11}$								
$CH_4$	$\textbf{2.82}\times \textbf{10}^{-7}$	$\textbf{9.21}\times \textbf{10}^{-\textbf{8}}$	$1.79\times10^{-7}$								

$$\begin{aligned} (\text{CO}_2)_t &= (\text{CO}_2)_0 \\ &\times \left[ 0.217 + 0.259 e^{\frac{-t}{1729}} + 0.338 e^{\frac{-t}{1851}} + 0.186 e^{\frac{-t}{1.186}} \right] \end{aligned} \tag{1}$$

$$(N_2 0)_t = (N_2 0)_0 \times \left[ e^{\frac{-t}{114}} \right]$$
 (2)

$$(CH_4)_t = (CH_4)_0 \times \left[e^{\frac{-t}{12}}\right]$$
(3)

where *t* is the number of years since the pulse emission,  $(GHG)_0$  is the mass of GHG initially emitted, and  $(GHG)_t$  is the mass of GHG remaining in the atmosphere at year *t*. These decay patterns of unit mass emissions of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> are shown in Fig. 1.

The time profiles of atmospheric mass of each GHG are then converted to time profiles of atmospheric concentration, based on the molecular mass of each GHG, the molecular mass of air estimated at 28.95 g/mole, and the total mass of the atmosphere estimated at  $5.148 \times 10^{21}$  g [11]. GHGs vary in their radiative efficiency, which determines their ability to accumulate heat. Per unit of mass, N<sub>2</sub>O traps the most heat, followed by CH<sub>4</sub> and then CO<sub>2</sub>. We estimate marginal changes in instantaneous radiative forcing due to the GHG concentration changes using the following equations [3,9,10]:

$$F_{\rm CO_2} = \frac{3.7}{\ln(2)} \times \ln\left\{1 + \frac{\Delta \rm CO_2}{\rm CO_{2ref}}\right\}$$
(4)

$$F_{N_2O} = 0.12 \times \left(\sqrt{\Delta N_2 O + N_2 O_{ref}}\right) - \sqrt{N_2 O_{ref}}\right) - f(M, N)$$
(5)

$$F_{CH_4} = 0.036 \times \left(\sqrt{\Delta CH_4 + CH_{4ref}} - \sqrt{CH_{4ref}} - f(M, N)\right)$$
(6)

where  $F_{GHG}$  is instantaneous radiative forcing in W/m<sup>2</sup> for each GHG,  $\Delta$ GHG is the change in atmospheric concentration of the GHG (in units of ppmv for CO<sub>2</sub>, and ppbv for N<sub>2</sub>O and CH<sub>4</sub>), CO<sub>2</sub>ref = 383 ppmv, N<sub>2</sub>O<sub>ref</sub> = 319 ppbv, CH<sub>4</sub>ref = 1774 ppbv, and *f*(M,N) is a function to compensate for the spectral absorption overlap between N<sub>2</sub>O and CH<sub>4</sub> [3,9,10]. In this analysis we assume minor marginal changes in GHG concentrations.

The estimated values of instantaneous radiative forcing are annual and global averages, allowing us to integrate across time and area to determine aggregate impacts. We estimate the cumulative radiative forcing occurring each year in units of W s/m<sup>2</sup> (or J/m<sup>2</sup>) by multiplying the instantaneous radiative forcing of each year by the number of seconds in a year. This operation converts the energy flow per unit of time of the radiative imbalance caused by GHGs into units of energy accumulated in the earth system per m<sup>2</sup> of surface area per year. The total accumulated indirect energy (J) is then estimated by integrating the cumulative radiative forcing per m<sup>2</sup> over the surface area of the tropopause, based on a mean radius of 6383 km. The accumulated indirect energy (J) for each year is then divided by the direct heat of combustion (J) to yield unitless ratios.

## 3. Results

Fig. 2 shows the ratios of the indirect energy accumulated by GHGs associated with the combustion of bituminous coal, diesel oil, and natural gas, compared to the direct heat energy released by the combustion. The amount of accumulated indirect energy depends on the amount of GHG emitted, thus the ratio of coal is higher than those of oil and natural gas because coal produces more GHGs per unit of combustion heat than do oil and natural gas. The ratios are not fixed, but continue to increase over time as additional energy is accumulated for as long as GHG remains in the atmosphere. The rate of increase is not linear but becomes less steep over time, as the atmospheric concentrations of the GHGs



Fig. 1. Modeled atmospheric decay of unit pulses of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub>.



**Fig. 2.** Ratio of the indirect energy accumulated in the earth system by GHGs associated with the combustion of coal, oil, and natural gas, compared to the direct heat energy released by the combustion. The dashed lines correspond to GHGs emitted as combustion products of the fuels; the solid lines correspond to GHGs emitted from combustion as well as from extracting, processing and transporting the fuels.

gradually decrease. Inclusion of full lifecycle GHG emissions, i.e. from combustion of the fuels as well as from extracting, processing and transporting the fuels, results in significantly greater indirect heat accumulation than combustion emission only.

Considering only the combustion emissions, 100 years after burning a unit of fuel the GHG emissions from coal will have accumulated about 129 units of indirect heat, while emissions from oil and natural gas will have accumulated about 101 and 75 units of heat, respectively. After 240 years, the values are about 246, 192, and 143 units for coal, oil, and gas, respectively. Considering full lifecycle emissions, 100 years after burning a unit of fuel the GHG emissions from coal will have accumulated about 197 units of indirect heat, while emissions from oil and natural gas will have accumulated about 143 and 123 units of heat, respectively. After 240 years, the values are about 316, 252, and 197 units for coal, oil, and gas, respectively. Fuel cycle emissions have relatively greater significance during earlier decades, because of the high radiative efficiency and shorter atmospheric residence time of CH<sub>4</sub> emissions from coal mine methane and natural gas leakage. Fuel cycle emissions are somewhat more significant for coal and natural gas than for oil, due largely to methane emissions from coal mines and natural gas leaks.

Considering only combustion emissions,  $CO_2$  is responsible for over 99% of the cumulative radiative forcing for coal and natural gas, with N<sub>2</sub>O and CH<sub>4</sub> being responsible for less than 1% (Table 2). Combustion of diesel oil results in proportionally slightly higher emissions of N<sub>2</sub>O and CH<sub>4</sub>, which together account for about 2– 4% of total accumulated energy. Considering full lifecycle

Table 2

Contributions of CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub> to total accumulated energy over time periods of 20, 100, and 240 years, considering combustion emissions and full lifecycle emissions.

	Bituminous coal			Diese	Diesel oil		Natural gas				
	CO <sub>2</sub> (%)	N <sub>2</sub> O (%)	CH4 (%)	CO <sub>2</sub> (%)	N <sub>2</sub> O (%)	CH4 (%)	CO <sub>2</sub> (%)	N <sub>2</sub> O (%)	CH4 (%)		
Combustion emissions only											
20 years	99.1	0.4	0.5	96.2	1.5	2.4	99.1	0.1	0.8		
100 years	99.4	0.5	0.2	97.6	1.5	0.9	99.6	0.1	0.3		
240 years	99.5	0.4	0.1	98.3	1.2	0.5	99.8	0.0	0.2		
Full lifecycle emissions											
20 years	41.4	0.2	58.5	64.9	0.9	34.2	40.8	0.0	59.2		
100 years	66.2	0.3	33.5	83.1	1.2	15.7	65.7	0.0	34.2		
240 years	78.8	0.3	20.9	90.1	1.0	8.9	78.6	0.0	21.4		

emissions, CH<sub>4</sub> emissions contribute much more significantly, particularly during earlier periods. After 20 years, CH<sub>4</sub> is responsible for almost 60% of total accumulated energy for coal and natural gas, due primarily to coal mine methane emissions and natural gas leakage from extraction and transport infrastructure. The significance of CH<sub>4</sub> reduces over time, as it gradually decays from the atmosphere while CO<sub>2</sub> remains in the atmosphere for longer periods.

#### 4. Discussion and conclusions

The relation between direct and indirect heat of fossil fuel combustion is time-dependent. While the indirect heat associated with GHG emissions continues to accumulate over time, the direct heat of combustion is released immediately when the fuel is burned. Although some of the direct heat may be temporarily stored in the thermal mass of other materials (e.g. water that is boiled by the fuel), and some of the heat energy may be converted to other forms of energy (e.g. electricity), virtually all of the available energy in the fuel will soon be released as heat into the environment.

We have used simple climate models to represent complex natural processes, resulting in inevitable uncertainties. In our calculations of radiative forcing we have assumed relatively minor marginal changes in atmospheric GHG concentrations, such that radiative efficiencies and atmospheric decay patterns of the gases remain constant. However, significant increases in the atmospheric concentration of  $CO_2$  can be expected during the coming decades and centuries. Increased atmospheric  $CO_2$  concentration will decrease the marginal radiative efficiency of  $CO_2$ , but will also decrease the marginal atmospheric decay rate of  $CO_2$ . These will have opposite and therefore offsetting effects on radiative forcing, thus we expect this uncertainty to be minor [12]. Nevertheless, taking into account the expected future trajectories of GHG concentrations would reduce this uncertainty.

We have estimated cumulative radiative forcing by integrating instantaneous radiative forcing over time. This is a simplification, as we ignore the feedback effect that the accumulated energy will have on future outgoing radiation. Radiative forcing is a measure of the radiative imbalance given that atmospheric temperatures remain unchanged. In fact, the radiative forcing calculated here will increase the heat energy accumulated in the earth system, leading to more outgoing longwave radiation and an eventual restoration of radiative balance. Since instantaneous radiative forcing does not account for this feedback effect, our results will therefore slightly overestimate the amount of accumulated heat.

There is some uncertainty in the emissions factors for both combustion emissions and fuel cycle emissions (Table 1), which vary over time and place. We have used IPCC default values for combustion emissions factors, which are broadly valid, but which are subject to minor variability due to fuel composition and combustion conditions [4]. For each type of fossil fuel (coal, oil, and natural gas) there is a strong correlation between the heat of combustion and the amount of  $CO_2$  produced during combustion, which are determined by the ratio of hydrogen to carbon atoms and on the types of organic compounds in the fuels [13]. We have used fuel cycle GHG emissions factors based on case studies of representative examples of extraction and processing of three fossil fuels [5–7]. These emissions are subject to regional variation due to differences in geology and technology, for example the methane emissions from coal fields and the type of equipment used for

extraction and transport of the fuels. The fuel cycle emissions analyzed here are based on conventional industrial techniques, although unconventional sourcing (e.g. hydraulic fracturing of natural gas wells, or synthetic crude oil from bitumen in oil sands) may result in additional GHG emissions [14,15]. These sources of variation would affect the lifecycle GHG emissions, thus altering the amount of indirect heat accumulated by the fuels.

Despite these uncertainties, the overall trends reported here appear to be robust. In summary, the direct release of heat due to combustion of fossil fuels is minor in relation to the indirect effect of heat accumulated by GHGs emitted during the combustion. Fuel cycle emissions resulting from extracting, processing, and transporting fossil fuels also contribute significantly to total lifecycle GHG emissions and radiative forcing. The quantity of heat accumulated by GHGs continues to increase over time, as additional energy is accumulated in the earth system as long as the GHGs remain in the atmosphere.

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#### References

- EIA (United States Energy Information Administration), Annual Energy Review 2011; 2012. <a href="http://www.eia.gov/aer">http://www.eia.gov/aer</a>> (accessed 06.02.13).
- [2] IEA (International Energy Agency. Key World Energy Statistics 2012; 2012. <a href="http://www.iea.org">http://www.iea.org</a> (accessed 06.02.13).
- [3] IPCC (Intergovernmental Panel on Climate Change). Climate change 2007: The physical science basis. Contribution of working group I to the fourth assessment report; 2007, <http://www.ipcc.ch> (accessed 06.02.13).
- [4] IPCC (Intergovernmental Panel on Climate Change). Guidelines for national greenhouse gas inventories; 2006, <a href="http://www.ipcc.ch">http://www.ipcc.ch</a> (accessed 06.02.2013).
- [5] NETL (National Energy Technology Laboratory). Life cycle analysis: Integrated Gasification Combined Cycle (IGCC) power plant. Report number DOE/NETL-403-110209; 2010.
- [6] NETL (National Energy Technology Laboratory). Development of baseline data and analysis of life cycle greenhouse gas emissions of petroleum-based fuels. Report number DOE/NETL-2009/1346; 2008.
- [7] NETL (National Energy Technology Laboratory). Life cycle analysis: Natural Gas Combined Cycle (NGCC) power plant. Report number DOE/NETL-403-110509; 2010.
- [8] Zetterberg L. A method for assessing the expected climatic effects from emission scenarios using the quantity radiative forcing. IVL Report B1111. Swedish Environmental Research Institute; Stockholm; 1993.
- [9] IPCC (Intergovernmental Panel on Climate Change). An introduction to simple climate models used in the IPCC second assessment report. IPCC technical paper II; 1997, <a href="http://www.ipcc.ch">http://www.ipcc.ch</a> (accessed 06.02.2013.
- [10] IPCC (Intergovernmental Panel on Climate Change). Climate change 2001: The scientific basis. Contribution of working group I to the third assessment report; 2001, <<u>http://www.ipcc.ch></u> (accessed 06.02.2013).
- [11] Trenberth K, Smith L. The mass of the atmosphere: A constraint on global analyses. J Climate 2005;18(6):864–75.
- [12] Caldeira K, Kasting JF. Insensitivity of global warming potentials to carbon dioxide emission scenarios. Nature 1993;366(6452):251–3.
- [13] Marland G, Andres RJ, Blasing TJ, Boden TA, Broniak CT, Gregg JS, Losey LM, Treanton K. Energy, industry, and waste management activities: An introduction to CO<sub>2</sub> emissions from fossil fuels. In: King et al. (editors). The First State of the Carbon Cycle Report (SOCCR): The North American carbon budget and implications for the global carbon cycle. Synthesis and assessment product 2.2. US climate change science program; 2007.
- [14] Howarth RW, Santoro R, Ingraffea A. Methane and the greenhouse-gas footprint of natural gas from shale formations. Climatic Change 2011;106(4):679–90.
- [15] Charpentier AD, Bergerson JA, MacLean HL. Understanding the Canadian oil sands industry's greenhouse gas emissions. Environmental Research Letters 2009;4:014005.