

REVIEW

## Global atmospheric methane: budget, changes and dangers

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A factor of 2.5 increase in the global abundance of atmospheric methane (CH<sub>4</sub>) since 1750 contributes 0.5 Wm<sup>-2</sup> to total direct radiative forcing by long-lived greenhouse gases (2.77 Wm<sup>-2</sup> in 2009), while its role in atmospheric chemistry adds another approximately 0.2 Wm<sup>-2</sup> of indirect forcing. Since CH<sub>4</sub> has a relatively short lifetime and it is very close to a steady state, reductions in its emissions would quickly benefit climate. Sensible emission mitigation strategies require quantitative understanding of CH<sub>4</sub>'s budget of emissions and sinks. Atmospheric observations of CH<sub>4</sub> abundance and its rate of increase, combined with an estimate of the CH<sub>4</sub> lifetime, constrain total global CH<sub>4</sub> emissions to between 500 and 600 Tg CH<sub>4</sub> yr<sup>-1</sup>. While total global emissions are constrained reasonably well, estimates of emissions by source sector vary by up to a factor of 2. Current observation networks are suitable to constrain emissions at large scales (e.g. global) but not at the regional to national scales necessary to verify emission reductions under emissions trading schemes. Improved constraints on the global CH<sub>4</sub> budget and its break down of emissions by source sector and country will come from an enhanced observation network for CH<sub>4</sub> abundance and its isotopic composition ( $\delta^{13}\text{C}$ ,  $\delta\text{D}$  (D = <sup>2</sup>H) and  $\delta^{14}\text{C}$ ). Isotopic measurements are a valuable tool in distinguishing among various sources that contribute emissions to an air parcel, once fractionation by loss processes is accounted for. Isotopic measurements are especially useful at regional scales where signals are larger. Reducing emissions from many anthropogenic source sectors is cost-effective, but these gains may be cancelled, in part, by increasing emissions related to economic development in many parts of the world. An observation network that can quantitatively assess these changing emissions, both positive and negative, is required, especially in the context of emissions trading schemes.

**Keywords:** global methane budget; climate; greenhouse gas mitigation; isotope geochemistry; biogeochemical cycles

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## 1. Introduction

Atmospheric methane ( $\text{CH}_4$ ) directly contributes  $0.5 \text{ Wm}^{-2}$  to total radiative forcing by long-lived greenhouse gases ( $2.77 \text{ Wm}^{-2}$  in 2009; update of [1]). Its role in atmospheric chemistry produces tropospheric ozone and stratospheric water vapour, which indirectly add approximately  $0.2 \text{ Wm}^{-2}$  [2] to its climate forcing. It has a short lifetime (approx. 9 years) compared with  $\text{CO}_2$  and is very close to a steady state [3], so reductions in its emissions would have immediate benefits for climate. Moreover, both palaeorecords and present-day studies suggest that some sources of emissions, such as wetlands and methane hydrates, may be subject to strong positive feedbacks on warming [4]. Methane is, therefore, very important in efforts to mitigate climate change.

Before mitigation strategies can be developed, its budget must be understood [5]. Methane is emitted to the atmosphere by natural (wetlands, oceans, termites and clathrates) and anthropogenic (fossil fuel exploitation, ruminant animals, rice agriculture, waste management and biomass burning) sources; emissions from many anthropogenic sources may be reduced cost-effectively. Initial assessments of  $\text{CH}_4$  emissions from plants were overestimated [6], and this is not likely to be a significant source [7]. The major removal processes from the atmosphere are reaction of  $\text{CH}_4$  with hydroxyl radicals ( $\text{OH}$ ) in the troposphere and stratosphere, minor reactions with atomic chlorine in the marine boundary layer and with electronically excited oxygen atoms ( $\text{O}(^1\text{D})$ ) in the stratosphere, and a minor but significant removal through oxidation by methanotrophic bacteria in soils.

The globally averaged  $\text{CH}_4$  dry air mole fraction in 2009 based on US National Oceanic and Atmospheric Administration (NOAA) measurements was 1794 ppb (we use ppb to abbreviate  $\text{nmol mol}^{-1}$ , dry air mole fraction).  $\text{CH}_4$  has increased by a factor of 2.5 from its pre-industrial value of approximately 700 ppb [8]. This increase, proportionately far greater than the parallel increase in  $\text{CO}_2$ , is driven mostly by increased anthropogenic emissions from fossil fuels, industry, agriculture (including biomass burning) and waste, but changes in  $\text{CH}_4$  lifetime and meteorological feedbacks may also have played a role.

The global distribution of  $\text{CH}_4$  is monitored by many national and university laboratories under the umbrella of the World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) programme. GAW provides the atmospheric chemistry component of the Global Climate Observing System.  $\text{CH}_4$  observations are reported to the World Data Centre for Greenhouse Gases (WDCGG) (<http://gaw.kishou.go.jp/wdcgg/>) by GAW participants. Measurements are reported either on the WMO  $\text{CH}_4$  mole fraction scale or with a conversion factor to ensure data are on that scale. This, along with ongoing quality control procedures, ensures that data from different national networks can be merged. Existing sampling coverage is sufficient to capture large-scale zonally averaged features, but it is not sufficient to verify national emission inventories. In particular, isotopic monitoring offers a powerful method of discriminating among sources, but as yet the data are very sparse.

## 2. The global methane budget: sources and sinks

Based on a pre-industrial  $\text{CH}_4$  atmospheric mole fraction of approximately 700 ppb and assuming the  $\text{CH}_4$  lifetime (approx. 9 year) has not changed substantially [9], total pre-industrial emissions were approximately 215 Tg  $\text{CH}_4 \text{ yr}^{-1}$ . This is a reasonable approximation for today's natural emissions, with the largest contribution from wetlands. Land-use changes have likely decreased natural emissions by only approximately 10 per cent [10]. Current estimates of  $\text{CH}_4$  emissions to the atmosphere from wetlands are approximately 150 Tg  $\text{CH}_4 \text{ yr}^{-1}$  [5], in good agreement with the estimate of Houweling *et al.* [10] for pre-industrial emissions. Emissions of  $\text{CH}_4$  from wetlands vary significantly from year to year depending on temperature and precipitation. Other natural sources include termites, oceans (approx. 20 Tg  $\text{CH}_4 \text{ yr}^{-1}$  each), wild fires and wild ruminant animals (approx. 5–10 Tg  $\text{CH}_4 \text{ yr}^{-1}$  each). The sum of these is consistent with estimates of natural emissions based on current and pre-industrial atmospheric  $\text{CH}_4$  abundance and the  $\text{CH}_4$  lifetime.

The global  $\text{CH}_4$  budget is summarized in table 1, with sources. The increase in the burden of atmospheric  $\text{CH}_4$  from pre-industrial to modern times is the result of increased emissions from fossil fuel exploitation, agriculture, waste management and anthropogenic biomass burning. Fossil fuel sources of methane are from coal extraction, crushing and processing, and abandoned mines; oil extraction and gas flaring; and especially from natural gas extraction, processing, transmission and distribution. Total emissions from this sector are estimated at approximately 110 Tg  $\text{CH}_4 \text{ yr}^{-1}$ . Agricultural sources are rice cultivation (approx. 30–40 Tg  $\text{CH}_4 \text{ yr}^{-1}$ ; by a similar process to  $\text{CH}_4$  emitted from wetlands) and ruminant animals (approx. 80–90 Tg  $\text{CH}_4 \text{ yr}^{-1}$ ). Waste sources are decomposition of biodegradable municipal solid waste in landfills and animal and human waste streams (approx. 50–60 Tg  $\text{CH}_4 \text{ yr}^{-1}$ ). Most biomass burning is initiated by humans for agricultural land clearing (seasonal grassland fires that spread from crop waste burning, especially in savannah Africa) and also for land-use change (e.g. burning after logging to clear land for eventual agricultural use). Total emissions are estimated to be 45–55 Tg  $\text{CH}_4 \text{ yr}^{-1}$ , but this source is highly variable interannually, largely according to meteorology (e.g. El Niño events). Together with emissions from wetlands, also meteorologically driven, burning is a major driver of interannual variability in  $\text{CH}_4$  growth rate.

The main loss process for atmospheric  $\text{CH}_4$  is oxidation in the troposphere initiated by reaction with OH, especially in the strong sunlight in the tropics. This oxidation, too, is highly influenced by meteorological variation. In the presence of sufficient  $\text{NO}_x$ , for example, in pollutant clouds from highly populated areas with strong transport emissions, this atmospheric oxidation process leads to tropospheric  $\text{O}_3$  formation, another strong greenhouse gas and atmospheric oxidant. Other processes that contribute minor  $\text{CH}_4$  removal from the troposphere are upward loss to the stratosphere, and oxidation by methanotrophic bacteria in soils, each contributing about 30 Tg  $\text{CH}_4 \text{ yr}^{-1}$  loss. Methanotrophs are also important in the oceans where they can oxidize into  $\text{CO}_2$  a significant fraction of  $\text{CH}_4$  emitted from seeps on the seabed, before it reaches the atmosphere. This may in future be a major uptake of widely dispersed emissions from

Table 1. Annual CH<sub>4</sub> emissions by source type for 1984–2003 from the electronic supplementary material in Bousquet *et al.* [5] in the middle column and for a range of years from 1997 to 2006 from Forster *et al.* [11] (Intergovernmental Panel on Climate Change (IPCC)); chemical sinks are scaled to total emissions based on Lelieveld *et al.* [12]. Units are Tg CH<sub>4</sub> yr<sup>-1</sup>, where 1 Tg = 10<sup>12</sup> g. Isotopic values are from a range of sources.

source	Bousquet (Tg yr <sup>-1</sup> )	IPCC (Tg yr <sup>-1</sup> )	δ <sup>13</sup> C (‰)	δD (‰)
<i>anthropogenic</i>				
energy	110 ± 13	74–106		–175 ± 10
coal and industry	47 ± 10		–35 ± 3	
gas	63 ± 9			
North Sea			–34 ± 3	
Siberia			–50 ± 3	
enteric fermentation <sup>a</sup>	90 ± 14	76–92		–305 ± 9
C4 diet			–49 ± 4	
C3 diet			–70 ± 4	
rice agriculture	31 ± 5	31–112	–62 ± 3	–323 ± 18
biomass burning <sup>b</sup>	50 ± 8	14–88		–210 ± 16
C4 vegetation			–17 ± 3	
C3 vegetation			–26 ± 3	
waste	55 ± 11	35–69		–293 ± 20
landfills			–53 ± 2	
domestic sewage			–57 ± 3	
animal waste			–58 ± 3	
<i>natural</i>				
wetlands	147 ± 15	100–231		
swamps	104 ± 12		–55 ± 3	
bogs and tundra	43 ± 8		–65 ± 5	
termites	23 ± 4	20–29		
oceans	19 ± 6	4–15		
total	525 ± 8	503–610	–52.9	–283 ± 13
<i>sinks</i>				
	Bousquet (Tg yr <sup>-1</sup> )	IPCC (Tg yr <sup>-1</sup> )		
troposphere	448 ± 1	428–511		
stratosphere	37 ± 1	30–45		
soil	21 ± 3	26–34		
total <sup>c</sup>	506	492–581		

<sup>a</sup>Contains a small amount of natural emissions from wild ruminants.

<sup>b</sup>Biomass burning includes biofuels and wild fires.

<sup>c</sup>For a burden of 4900 Tg CH<sub>4</sub> in 2003, implies  $\tau \approx 9.4$  yr.

seabed hydrates, which store methane made in the seabed both by anaerobic biological methanogenesis in shallow sediment and by geological heating at deeper levels.

Reaction with OH is the largest term in the global CH<sub>4</sub> budget, so small changes in OH can result in significant variability in CH<sub>4</sub> growth rate.

While total global emissions of CH<sub>4</sub> are constrained reasonably well by atmospheric observations and estimates of its lifetime ( $\pm 15\%$ ), uncertainties on emissions from individual sources are larger (up to a factor of 2), and they are poorly constrained by the current atmospheric observation network.

### **3. Vulnerability of the methane budget to global climate change: past and present**

Measurements of CH<sub>4</sub> mole fractions in air extracted from ice cores (e.g. [13]) show that the atmospheric CH<sub>4</sub> mole fraction during cold glacial periods was approximately 350 ppb; this is half what is recorded during warm interglacial periods, approximately 700 ppb. Measurements of CH<sub>4</sub> isotopic composition ( $\delta^{13}\text{C}$  and  $\delta\text{D}$ ) from the same ice cores combined with changes in the difference in CH<sub>4</sub> between Greenland and Antarctic ice cores for these periods suggest that changes in emissions from Boreal wetlands are the main drivers of the factor of 2 change in atmospheric CH<sub>4</sub> burden [14]. Colder temperatures and coverage of wetlands by continental ice sheets reduced CH<sub>4</sub> emissions to near zero during glacial periods [15]. Although changes in emissions from Arctic hydrates may have also contributed to the increasing burden of atmospheric CH<sub>4</sub>, support for a strong increase in wetland emissions also comes from relative changes in the <sup>14</sup>C content of CH<sub>4</sub> in air sealed in ice during the Younger Dryas–Preboreal transition [4,16].

Palaeoclimate records show strong coupling of climate with atmospheric methane abundance [4,13]. This is cause for concern about the impact of climate change on modern atmospheric CH<sub>4</sub> abundance. The rapidly warming Arctic (e.g. <http://maps.grida.no/go/graphic/trends-in-arctic-temperature-1880-2006>) contains widespread wetlands that respond immediately to warming. There are approximately 1000 Pg C in the top 3 m of Arctic land surface [17], and the possibility of significant thermokarst emissions is well documented [18]. The Arctic Ocean is warming with rapid loss of sea ice. Submarine plumes of methane were recently observed from the edge of the marine clathrate stability field [19]. These are, in part, a response to the warming of the West Spitsbergen current (i.e. incoming Atlantic water), but the impact of Arctic warming remains unknown, though it is probably still small in 2008 (R. Fisher 2008, unpublished results). Ignoring sediment on the continental slopes, there is additional CH<sub>4</sub> in hydrates on shallow Arctic continental shelves with an estimated 30–170 Pg CH<sub>4</sub>. Terrestrial permafrost soils may contain an estimated 2–65 Pg of CH<sub>4</sub> in clathrate. Uncertainties on these pools are large, despite significant reductions in their magnitudes based on recent data [20]. Using two IPCC greenhouse gas emission scenarios in the Community Climate System Model (v. 3) with explicit treatment of frozen soil processes, Lawrence & Slater [21] found that between 50 and 90 per cent of near-surface permafrost could melt by 2100. Although the large magnitude of these changes has been disputed [22,23] and methanotrophic uptake would probably convert most CH<sub>4</sub> produced to CO<sub>2</sub>, there is clearly potential for increased future CH<sub>4</sub> emissions.

Thus, there are large positive greenhouse feedbacks on climate warming in high northern latitudes. The wetland feedback may be immediate and strong. Temperature increases will surely result in greater CH<sub>4</sub> production and increases in water supply from melting abundant ice. In the longer term, changes in hydrology must also be assessed to determine the net effect on CH<sub>4</sub> emissions. We speculate that, in the short term (few decades), melting permafrost will result in larger wetland areas; when combined with warmer temperatures, this will result in increased CH<sub>4</sub> emissions. The impact of a warming Arctic will

probably only slowly increase emissions from hydrates except where pools or reservoirs of free gas are released when an overlying layer of impermeable clathrate decays.

In the boreal forests, south of the tundra, methane emissions will respond to changes in fire frequency, closely coupled to landscape wetness and temperature. Fire frequency may increase as climate warms and the difference between precipitation and evaporation changes.

In addition to natural sources and the impact of human activity on natural or quasi-natural sources, direct anthropogenic emissions are linked to meteorology. In particular, wider use of heating and air-conditioning in rapidly developing nations in Asia will add to the global CH<sub>4</sub> burden. For example, in China, where coal provides approximately 70 per cent of primary energy production, coal mining increased by more than a factor of 2 from 2000 to 2008 [24]. CH<sub>4</sub> formed during coalification is emitted when the coal is mined. Hot summers and cold winters will sharply affect energy consumption patterns. Overall, meteorology plays a major role in year-on-year fluctuations [25].

#### 4. CH<sub>4</sub> observational network

Maps of sites reporting *in situ* atmospheric CH<sub>4</sub> mole fractions and  $\delta^{13}\text{C}$  and  $\delta\text{D}$  in CH<sub>4</sub> can be obtained from the WMO WDCGG maintained by the Japan Meteorological Agency ([http://gaw.kishou.go.jp/cgi-bin/wdcgg/map\\_search.cgi](http://gaw.kishou.go.jp/cgi-bin/wdcgg/map_search.cgi)). Most records of CH<sub>4</sub> mole fraction,  $\delta\text{D}$ , and  $\delta^{13}\text{C}$  are from discrete samples measured at a central laboratory. Some sites have *in situ* analysers for quasi-continuous measurements of CH<sub>4</sub> mole fraction. At Royal Holloway University London (RHUL), Egham (51°25.6' N, 0°33.7' W, 32 km WSW of the centre of London), UK, quasi-continuous measurements of  $\delta^{13}\text{C}_{\text{CH}_4}$  are carried out in campaigns to monitor London urban emissions.

To ensure that measurements of CH<sub>4</sub> mole fraction from different networks meet the WMO GAW compatibility target of  $\pm 2$  ppb [26] and can be included in model studies without causing bias, a common standard scale maintained at NOAA is used [27]. But, this is not enough to provide datasets capable of constraining large-scale chemical transport models; quality control strategies such as 'round-robin' comparisons of air in cylinders, same air comparisons (where two laboratories measure air from the same sample), and comparison of simultaneous measurements using different methods, among other approaches, are used. Without these comparisons, modelling work has little value. Currently, most programmes that measure atmospheric CH<sub>4</sub> are involved in comparisons of measurements [28,29].

Most measurements of CH<sub>4</sub> mole fraction have been made by gas chromatography (GC) with flame ionization detection. Typical repeatability of the method is better than  $\pm 2$  ppb. New optical techniques using off-axis integrated cavity output spectroscopy or cavity ring down spectroscopy offer better repeatability (approx. 0.25 ppb), large dynamic range and faster response times without the need for expendable gases (N<sub>2</sub> carrier gas and fuel gases). They also require less technical expertise to operate at scientifically useful levels of repeatability and are much more robust and reliable (e.g. after power outage).  $\delta^{13}\text{C}_{\text{CH}_4}$  is now typically measured with continuous flow GC/isotope ratio mass spectrometry (CF-GCIRMS). Repeatability for CF-GCIRMS is now

approximately  $\pm 0.05\%$  for  $\delta^{13}\text{C}$  [30], capable of identifying remote sources of  $\text{CH}_4$  by back-trajectory analysis, and observing seasonality. This precision compares approximately to  $\pm 0.03\%$  for conventional techniques. For  $\delta\text{D}_{\text{CH}_4}$ , repeatability is approximately  $\pm 1\%$ .

Various *in situ* sampling platforms are used. Most time series of  $\text{CH}_4$  mole fraction and isotopic composition are from discrete flask samples collected at sampling locations on land and from ships, supplemented by a small number of sites making quasi-continuous measurement observations. Historically, continuous measurements have been made at global observatories from sampling heights of 15–40 m above ground, usually from the background (marine) air sector, but more recent studies have sampled from multiple levels up to approximately 500 m on tall radio and television towers to assess emissions from heavily populated regions. Tower sampling increases the footprint area that influences the observations and makes for easier comparisons with modelled meteorology, because the quality of meteorology decreases closer to the surface. Measurement of the vertical gradient in  $\text{CH}_4$  from tall towers also tests the ability of models to reproduce the gradient. Systematic measurements are also made from aircraft to capture the vertical distribution of  $\text{CH}_4$  and to monitor the free troposphere.

Measurements are mostly made by developed countries and where logistics make them feasible. This results in large gaps in sampling, many of them in areas of strong  $\text{CH}_4$  emissions, such as the tropics, South Asia and Siberia. In particular, there are only a handful of sites frequently (e.g. hourly) measuring  $\text{CH}_4$  in the tropics and virtually no long-term land-based time series. Most information from the tropics is from US NOAA flask time series. To supplement the information from tropical latitudes, information has come from retrievals of total column  $\text{CH}_4$  from irradiances collected by spectrometers on satellites such as the Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) onboard the Environmental Satellite (ENVISAT) [31,32]. This is very powerful in its geographical coverage. However, SCIAMACHY relies on reflected sunlight, so  $\text{CH}_4$  column-averaged mole fractions cannot be retrieved at high latitudes during winter, nor anywhere when skies are cloudy (i.e. during specific weather patterns) nor at night. However, there is an urgent need for ground validation by much higher accuracy *in situ* time series from the tropics. Recent estimates of  $\text{CH}_4$  emissions for the tropics made with and without SCIAMACHY column averages obtain about the same total emissions for the tropics, but the better spatial coverage of the satellite retrievals results in more reasonable spatial distributions for the emissions [33] when column averages are included.

## 5. Global methane in 2010—observations

Globally averaged  $\text{CH}_4$  mole fractions and their instantaneous growth rate determined from sites in the NOAA global cooperative air sampling network are plotted in figure 1 for 1983–2009. Three features are notable, as follows.

- (i) The growth rate of  $\text{CH}_4$  decreased from the start of the record until the late 1990s. Dlugokencky *et al.* [34] interpreted this behaviour as an approach to a steady state, where emissions were approximately constant.
- (ii) From 1999 to 2006, globally averaged  $\text{CH}_4$  was relatively constant.

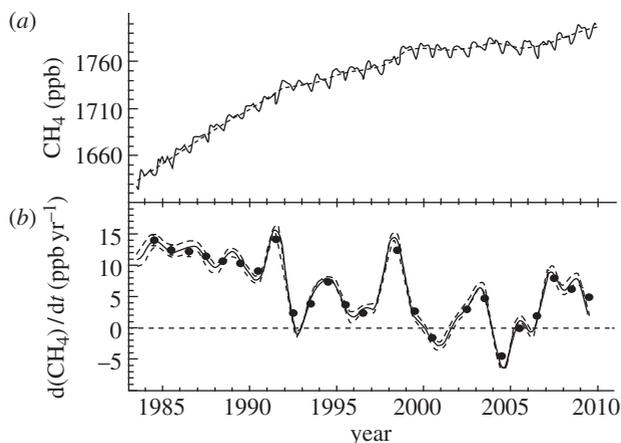


Figure 1. (a) Globally averaged  $\text{CH}_4$  dry air mole fractions determined from weekly samples in the NOAA Global Cooperative Air Sampling Network; dashed line is a deseasonalized trend fitted to the global averages. The seasonal cycle is a convolution of seasonal cycles from Northern and Southern Hemisphere sites driven by seasonality in reaction rates of  $\text{CH}_4$  with OH and emissions from some sources (wetlands, rice production and biomass burning), and impacts of meteorology. (b) Globally averaged instantaneous  $\text{CH}_4$  growth rate calculated from the dashed line in (a). Uncertainties are  $\pm 1\sigma$ . Circles are annual increases calculated from 1 January in one year to 1 January in the next year.

- (iii) Superimposed onto these long-term signals is significant interannual variability, with sharp changes in 1991/1992 related to the eruption of Mt Pinatubo and the economic collapse in the former Soviet Union (e.g. [35,36]), in 1997/1998 related to conditions during a strong El Niño [37] and in 2007–2009 [3,38].

This variability in growth rate, when combined with other information, can be useful in testing our understanding of specific processes. The increases in  $\text{CH}_4$  growth rate in 2007–2009 raise concerns that strong climate feedbacks in the Arctic may already be activated and affecting the global burden of atmospheric  $\text{CH}_4$ . However, analysis of  $\delta^{13}\text{C}$  in  $\text{CH}_4$ , CO mole fractions, and tropical precipitation suggest these increases are, so far, meteorologically driven.

A sensitive tool to locate changing emissions, especially in the Arctic, is the study of  $\text{CH}_4$  spatial gradients. In figure 2, differences between northern ( $53\text{--}90^\circ\text{N}$ ) and southern ( $53\text{--}90^\circ\text{S}$ ) annual mean  $\text{CH}_4$  mole fractions, referred to as the inter-polar difference (IPD), are plotted as a function of time (circles). Triangles are IPD calculated with a transport model (TM3) using inventory estimates of anthropogenic emissions and constant natural emissions (updated from [34]). The decrease in IPD from 1991 to 1992 by approximately 10 ppb, which has not recovered, is attributed to the collapse of the economy of the former Soviet Union (including its large coal industry) and the subsequent heavy investment by the Russian gas industry in cutting leaks. Inventories imply that the decrease in  $\text{CH}_4$  emissions was of order of  $10\text{ Tg CH}_4\text{ yr}^{-1}$ . If the inventories are accurate and the observed change in IPD resulted from this change in anthropogenic emissions, a persistent signal could be observed with the current measurement network from changes in Arctic wetland emissions of order of  $3\text{ Tg CH}_4\text{ yr}^{-1}$ , or about 10 per cent of total northern wetland emissions.

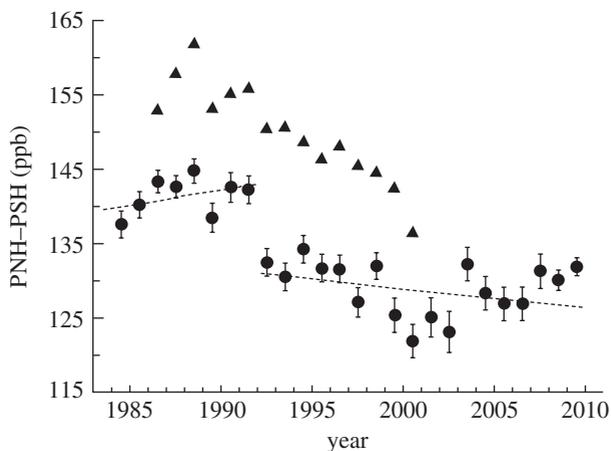


Figure 2. Differences between northern (53–90°N) and southern (53–90°S) observed annual mean CH<sub>4</sub> mole fractions (circles) as a function of time. Dashed lines are linear least squares fits to the time periods 1984–1991 and 1992–2009. Triangles are differences calculated from a three-dimensional atmospheric transport model.

## 6. Isotopic monitoring

Routine monitoring of  $\delta^{13}\text{C}$  in CH<sub>4</sub> in ambient air is presently very limited, mainly carried out by the University of Colorado, Institute of Arctic and Alpine Research (INSTAAR), for the US NOAA network of sites, by New Zealand's National Institute of Water and Atmospheric Research, by the University of Heidelberg in Germany and by RHUL in the UK.

Isotopic measurements carry powerful information about sources because they are enriched or depleted in  $^{13}\text{C}$  or D relative to ambient background air, which typically has  $\delta^{13}\text{C} \approx -47\text{‰}$  and  $\delta\text{D} \approx -85\text{‰}$ . CH<sub>4</sub> formed at high temperatures (combustion) is enriched in the heavier isotope and CH<sub>4</sub> from biogenic origin is depleted. Wetlands have signatures that vary between  $-70$  and  $-60\text{‰}$  at high northern latitudes and between  $-60$  and  $-50\text{‰}$  in tropical climates. Because of different photosynthetic pathways, C3 and C4 plants have very different organic carbon isotope signatures, so, when these are either burned or digested, the CH<sub>4</sub> released has different isotopic signatures. Therefore, savannah grassland burning (C4) releases CH<sub>4</sub> with  $\delta^{13}\text{C}$  of  $-20$  to  $-15\text{‰}$ , whereas boreal forest burning releases CH<sub>4</sub> at  $-30$  to  $-25\text{‰}$ . Similarly, ruminants digesting C4 plants give off CH<sub>4</sub> at  $-55$  to  $-50\text{‰}$ , whereas those eating C3 plants give off  $-65$  to  $-60\text{‰}$  CH<sub>4</sub>. The natural gas industry produces CH<sub>4</sub> of variable isotopic signature depending on the formation temperature of the gas reservoir (biogenic or thermogenic). The resultant gas distribution networks contain gas at close to  $-50\text{‰}$  in the Russian pipelines, around  $-35\text{‰}$  for the North Sea and can reach  $-25\text{‰}$ .

High-precision isotopic monitoring can provide potent new constraints on the regional and latitudinal CH<sub>4</sub> source mix. Coupled with back-trajectory analysis, precise isotopic measurement can provide an important discriminant in identifying specific emissions by time, location and source type. For example, Fisher *et al.* [39] used measurements of CH<sub>4</sub> and its isotopic composition to

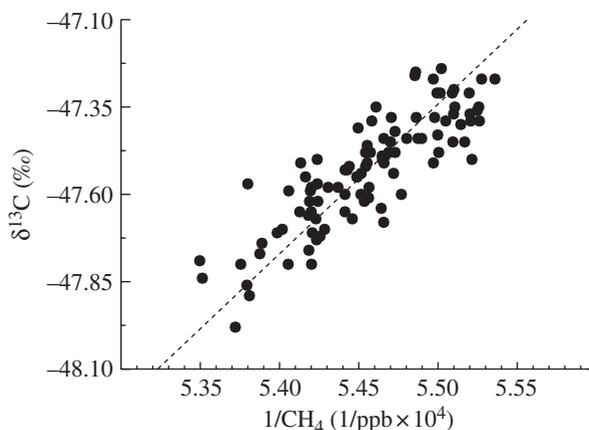


Figure 3. Plot of  $\delta^{13}\text{C}_{\text{CH}_4}$  versus inverse  $\text{CH}_4$  mole fractions from samples collected at sea in the North Atlantic and from Ny-Ålesund, Svalbard, during summer, 2008. The intercept of the plot gives the isotopic signature of the source responsible for enhancements in  $\text{CH}_4$ , which is  $-64.6\text{‰}$ , consistent with wetland emissions.

constrain Arctic emissions. Inputs of  $\text{CH}_4$  at high northern latitudes have distinct  $\delta^{13}\text{C}$  signatures, from  $-28\text{‰}$  for boreal forest burning emissions,  $-50$  to  $-35\text{‰}$  for natural gas emissions,  $-60$  to  $-50\text{‰}$  for  $\text{CH}_4$  hydrates,  $-69$  to  $-62\text{‰}$  for wetlands and  $-80$  to  $-50\text{‰}$  for the variable thermokarst  $\text{CH}_4$  (e.g. [18]). In figure 3,  $\delta^{13}\text{C}$  in  $\text{CH}_4$  is plotted against the inverse  $\text{CH}_4$  mole fraction (Keeling plot) from observations at high northern latitudes. The  $y$ -intercept of this plot gives the isotopic composition of the source for enhanced  $\text{CH}_4$  ( $-65\text{‰}$ ), suggesting a dominant summer wetland contribution. Similar results have been obtained in Canada. Based on systematic measurements of  $\text{CH}_4$  and its stable isotopes ( $\delta^{13}\text{C}$  and  $\delta\text{D}$ ), winter elevations in  $\text{CH}_4$  mole fraction at Lac La Biche, Canada, have source signatures of  $-60\text{‰}$  for  $\delta^{13}\text{C}$  and  $-300\text{‰}$  for  $\delta\text{D}$  (J. White 2010, unpublished INSTAAR data). Unpublished data (2009) from Spitsbergen also show much heavier (less negative)  $\delta^{13}\text{C}_{\text{CH}_4}$  in winter when wetlands are frozen and gasfield production is active [39].

Recent focus has been on the isotopes of Arctic  $\text{CH}_4$  sources because of their potential instability and role in past climate change. More work is required for other sources too, particularly in the tropics, China and India, where isotopic techniques can distinguish between major sources, such as rice production and coal mining.

## 7. Prospects for reducing emissions

Methane is an extremely attractive and relatively inexpensive target for short-term reductions in greenhouse warming. Reductions in  $\text{CH}_4$  emissions can often be made cost-effectively, or at little cost, from agriculture, energy sectors (underground coal mines, oil and gas) and landfills by capturing  $\text{CH}_4$  and using it as a source of energy. The international Methane to Markets Partnership ([www.methanetomarkets.org](http://www.methanetomarkets.org)) organizes technical and market expertise to capture  $\text{CH}_4$  and use it as an energy source. For example, opportunities to

reduce emissions from the oil and gas industry come from upgrading technology, improving operating procedures and actively finding and fixing leaks. With global emission estimates of approximately  $50 \text{ Tg CH}_4 \text{ yr}^{-1}$  from this sector, and an estimated value of the leaked gas at approximately US\$150 million per  $\text{Tg CH}_4$  (based on the late-2009 US wellhead price of US\$3 per  $1000 \text{ ft}^3$ ), cost savings can be substantial.

In the agricultural sector, recovery and utilization of  $\text{CH}_4$  from anaerobic digestion of animal waste (pigs and cattle) and reducing the number of  $\text{CH}_4$ -producing microbes during enteric fermentation in ruminants provide viable opportunities for  $\text{CH}_4$  emission reductions. Landfill gas is approximately 50 per cent  $\text{CH}_4$ , and it can be exploited by collecting it, processing it and then distributing it to end-users to produce electricity or heat. Coal mine  $\text{CH}_4$  is a hazard and must be removed for safe operation of a mine. Rather than venting it from a mine ventilation system, it can be captured and used. Even low-concentration  $\text{CH}_4$  has profitable end uses.

Emission reductions can also be achieved by eliminating generation of  $\text{CH}_4$ ; for example, by diverting organic materials normally sent to landfills to aerobic composting or incineration, and by improved fire management for agricultural and grazing lands. Diversion of organic matter from landfills to composting reduces  $\text{CH}_4$  emissions and has other environmental benefits including end-product use as a soil amendment that improves moisture retention and carbon storage, and reduces need for inorganic fertilizer, potentially reducing  $\text{N}_2\text{O}$  emissions.

## 8. Use of *in situ* measurements and remote-sensing to validate declared methane emissions

Emission reduction needs validation. This means that both natural and anthropogenic sources need to be located and characterized by location, type and time/seasonality. Diagnostic studies of emissions using atmospheric observations lead to better emission models that can be used to predict responses to changing climate and to validate emissions declarations under the UN Framework Convention on Climate Change (UNFCCC). Simulations using atmospheric chemical transport models are routinely compared with atmospheric observations to assess our understanding of emission processes. Critical to the success of all modelling is a rigorous assessment of the quality of the data as discussed earlier.

Modelling studies can help to answer a basic question: are the distribution, seasonality and magnitude of emissions assessed by inventories consistent with the observed distribution and seasonal cycle of  $\text{CH}_4$  after accounting for transport? This approach was used by Fung *et al.* [40] to eliminate specific scenarios of emissions. A more sophisticated approach involves the use of inverse methods to estimate fluxes from observations. With this method, simulations of atmospheric  $\text{CH}_4$  distribution made with a chemical transport model are compared with observations. An emissions distribution is then solved for that gives optimal agreement between the observations and the simulations. In either case, *a priori* estimates of emissions from inventories or process models are usually needed.

It is particularly useful to employ assimilation methods that use many different data streams (e.g. *in situ* measurements, eddy covariance fluxes, observation of multiple parameters that influence emissions and satellite retrievals). Assimilations can be used from regional to global scales by using different transport models, so they can also be used to verify changes in emissions resulting from mitigation schemes.

Bergamaschi *et al.* [41] used an atmospheric transport model at  $1^\circ \times 1^\circ$  resolution with observed atmospheric  $\text{CH}_4$  mole fractions to estimate national-level emissions for Europe. They found that emissions reported by some nations to the UNFCCC were underestimated by 50–90% compared with the model inversion, and, in one instance, emissions were overestimated. Updating this, Bergamaschi *et al.* [42] found that inversion modelling implied that anthropogenic emissions of  $\text{CH}_4$  from northwest Europe in the period 2001–2006 were 40 per cent greater than reported to the UNFCCC. This is a significant discrepancy and emphasizes the need for verification of emissions. In North America, Kort *et al.* [43] used a Lagrangian particle dispersion model with measurements of atmospheric  $\text{CH}_4$  from aircraft for May–June 2003 and found that North American inventories compiled by the Emissions Database for Global Atmospheric Research and Global Emissions Inventory Activity are reasonably consistent with observations, at least for the limited temporal and spatial extent of their study.

One approach to slow global warming by reducing greenhouse gas emissions is through emissions trading schemes. As yet there is no atmospheric verification of emissions trading, despite the already significant scale of the market. If verification is introduced to check fraud, demands on observation networks will increase under these schemes as atmospheric observations will be used to verify inventory-based estimates of emissions and how they change with time. Current networks are suitable for assessing emissions over large scales, but better coverage by continuous measurements and more isotopic monitoring are needed at continental, regional and local scales if emissions trading is to be verified.

## 9. Conclusions

Reductions in emissions of anthropogenic  $\text{CH}_4$  will have a small, but rapid, impact on the rate of increase in radiative forcing. While methane's budget of sources and sinks can be accurately quantified at global scales with the current network of observations, knowledge of national, regional and local budgets is still limited. Despite this, it is clear that reducing emissions from agriculture, energy production and landfills can be achieved cost-effectively. With the current observation network we can neither accurately assess the magnitude of reduced emissions nor accurately assess the role of rapidly developing economies in Asia on the global  $\text{CH}_4$  budget.

Efforts to reduce anthropogenic emissions may be, in part, cancelled by nature, particularly in the Arctic. Rapid warming there has the potential to release large stores of carbon from permafrost and  $\text{CH}_4$  hydrates. Isotopic measurements can provide strong constraints on the relative roles of anthropogenic versus natural emissions to observed increases in atmospheric  $\text{CH}_4$ . Isotopes were especially

useful to help explain the CH<sub>4</sub> increase during 2007 and 2008, at least in the Arctic. To understand the processes leading to changing emissions, better *in situ* monitoring of CH<sub>4</sub> mole fractions and isotopic composition is required.

### References

- 1 Hofmann, D. J., Butler, J. H., Dlugokencky, E. J., Elkins, J. W., Masarie, K., Montzka, S. A. & Tans, P. 2006 The role of carbon dioxide in climate forcing from 1979–2004: introduction of the Annual Greenhouse Gas Index. *Tellus B* **58**, 614–619. (doi:10.1111/j.1600-0889.2006.00201.x)
- 2 Hansen, J. E. & Sato, M. 2001 Trends of measured climate forcing agents. *Proc. Natl Acad. Sci. USA* **98**, 14 778–14 783. (doi:10.1073/pnas.261553698)
- 3 Dlugokencky, E. J. et al. 2009 Observational constraints on recent increases in the atmospheric CH<sub>4</sub> burden. *Geophys. Res. Lett.* **36**, L18803. (doi:10.1029/2009GL039780)
- 4 Nisbet, E. G. & Chappellaz, J. 2009 Shifting gear, quickly. *Science* **324**, 477–478. (doi:10.1126/science.1172001)
- 5 Bousquet, P. et al. 2006 Contribution of anthropogenic and natural sources to atmospheric methane variability. *Nature* **443**, 439–443. (doi:10.1038/nature05132)
- 6 Keppler, F., Hamilton, J. T. G., Brass, M. & Röckmann, T. 2006 Methane emissions from terrestrial plants under aerobic conditions. *Nature* **439**, 187–191. (doi:10.1038/nature04420)
- 7 Nisbet, R. E. R. et al. 2009 Emission of methane from plants. *Proc. R. Soc. B* **276**, 1347–1354. (doi:10.1098/rspb.2008.1731)
- 8 Etheridge, D. M., Steele, L. P., Francey, R. J. & Langenfelds, R. L. 1998 Atmospheric methane between 1000 A.D. and present: evidence of anthropogenic emissions and climatic variability. *J. Geophys. Res.* **103**, 15 979–15 993. (doi:10.1029/98JD00923)
- 9 Lelieveld, J., Peters, W., Dentener, F. J. & Krol, M. C. 2002 Stability of tropospheric hydroxyl chemistry. *J. Geophys. Res.* **107**, 4715. (doi:10.1029/2002JD002272)
- 10 Houweling, S., Dentener, F. & Lelieveld, J. 2000 Simulation of preindustrial atmospheric methane to constrain the global source strength of natural wetlands. *J. Geophys. Res.* **105**, 17 243–17 255. (doi:10.1029/2000JD00193)
- 11 Forster, P. et al. 2007 Changes in atmospheric constituents and in radiative forcing. In *Climate change 2007: the physical science basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* (eds S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. Averyt, M. Tignor & H. Miller). Cambridge, UK: Cambridge University Press.
- 12 Lelieveld, J., Crutzen, P. J. & Dentener, F. J. 1998 Changing concentration, lifetime and climate forcing of atmospheric methane. *Tellus* **50B**, 128–150. (doi:10.1034/j.1600-0889.1998.t01-1-00002.x)
- 13 Brook, E. J. et al. 2000 On the origin and timing of rapid changes in atmospheric methane during the last glacial period. *Global Biogeochem. Cycles* **14**, 559–572. (doi:10.1029/1999GB001182)
- 14 Dällenbach, A., Blumier, T., Flückiger, J., Stauffer, B., Chappellaz, J. & Raynaud, D. 2000 Changes in the atmospheric CH<sub>4</sub> gradient between Greenland and Antarctica during the Last Glacial and the transition to the Holocene. *Geophys. Res. Lett.* **27**, 1005–1008. (doi:10.1029/1999GL010873)
- 15 Fischer, H. et al. 2008 Changing boreal methane sources and constant biomass burning during the last termination. *Nature* **452**, 864–867. (doi:10.1038/nature06825)
- 16 Petrenko, V. V. et al. 2009 <sup>14</sup>CH<sub>4</sub> Measurements in Greenland ice: investigating last glacial termination CH<sub>4</sub> sources. *Science* **324**, 506–508. (doi:10.1126/science.1168909)
- 17 Tarnocai, C., Canadell, J. G., Schuur, E. A. G., Kuhry, P., Mazhitova, G. & Zimov, S. 2009 Soil organic carbon pools in the northern circumpolar permafrost region. *Global Biogeochem. Cycles* **23**, GB2023. (doi:10.1029/2008GB003327)
- 18 Walter, K. M., Zimov, S. A., Chanton, J. P., Verbyla, D. & Chapin III, F. S. 2006 Methane bubbling from Siberian thaw lakes as a positive feedback to climate warming. *Nature* **443**, 71–75. (doi:10.1038/nature05040)

- 19 Westbrook, G. K. *et al.* 2009 Escape of methane gas from the seabed along the West Spitsbergen continental margin. *Geophys. Res. Lett.* **36**, L15608. (doi:10.1029/2009GL039191)
- 20 Milkov, A. V. 2004 Global estimates of hydrate-bound gas in marine sediments: how much is really out there? *Earth Sci. Rev.* **66**, 183–197. (doi:10.1016/j.earscirev.2003.11.002)
- 21 Lawrence, D. M. & Slater, A. G. 2005 A projection of severe near-surface permafrost degradation during the 21st century. *Geophys. Res. Lett.* **32**, L24401. (doi:10.1029/2005GL025080)
- 22 Burn, C. R. & Nelson, F. E. 2006 Comment on ‘A projection of severe near-surface permafrost degradation during the 21st century’ by David M. Lawrence and Andrew G. Slater. *Geophys. Res. Lett.* **33**, L21503. (doi:10.1029/2006GL027077)
- 23 Delisle, G. 2007 Near-surface permafrost degradation: how severe during the 21st century? *Geophys. Res. Lett.* **34**, L09503. (doi:10.1029/2007GL029323)
- 24 BP. 2009 BP statistical review of world energy. See <http://www.bp.com/statisticalreview>.
- 25 Warwick, N. J., Bekki, S., Law, K. S., Nisbet, E. G. & Pyle, J. A. 2002 The impact of meteorology on the interannual growth rate of atmospheric methane. *Geophys. Res. Lett.* **29**, 1947–1950. (doi:10.1029/2002GLO/5282)
- 26 WMO. 2006 Global atmosphere watch. In *Proc. 13th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques, Boulder, CO, 19–22 September 2005*. GAW report no. 168; WMO TD no. 1359. See <http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html>.
- 27 Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W. & Steele, L. P. 2005 Conversion of NOAA atmospheric dry air CH<sub>4</sub> mole fractions to a gravimetrically prepared standard scale. *J. Geophys. Res.* **110**, D18306. (doi:10.1029/2005JD006035)
- 28 Masarie, K. A. *et al.* 2001 NOAA/CSIRO flask air intercomparison experiment: a strategy for directly assessing consistency among atmospheric measurements made by independent laboratories. *J. Geophys. Res.* **106**, 20 445–20 464. (doi:10.1029/2000JD000023)
- 29 Manning, A. C. *et al.* 2009 Final report on CarboEurope intercomparison programme. See [http://cucumbers.uea.ac.uk/documents/CucumberFinalReport\\_Final.pdf](http://cucumbers.uea.ac.uk/documents/CucumberFinalReport_Final.pdf).
- 30 Fisher, R. *et al.* 2006 High-precision, automated stable isotope analysis of atmospheric methane and carbon dioxide using continuous-flow isotope-ratio mass spectrometry. *Rapid Commun. Mass Spectrom.* **20**, 200–208. (doi:10.1002/rcm.2300)
- 31 Frankenberg, C., Meirink, J. F., van Weele, M., Platt, U. & Wagner, T. 2005 Assessing methane emissions from global space-borne observations. *Science* **308**, 1010–1014. (doi:10.1126/science.1106644)
- 32 Frankenberg, C., Warneke, T., Butz, A., Aben, I., Hase, F., Spietz, P. & Brown, L. R. 2008 Pressure broadening in the 2ν<sub>3</sub> band of methane and its implication on atmospheric retrievals. *Atmos. Chem. Phys.* **8**, 5061–5075. (doi:10.5194/acp-8-5061-2008)
- 33 Bergamaschi, P. *et al.* 2009 Inverse modeling of global and regional CH<sub>4</sub> emissions using SCIAMACHY satellite retrievals. *J. Geophys. Res.* **114**, D22301. (doi:10.1029/2009JD012287)
- 34 Dlugokencky, E. J., Houweling, S., Bruhwiler, L., Masarie, K. A., Lang, P. M., Miller, J. B. & Tans, P. P. 2003 Atmospheric methane levels off: temporary pause or a new steady-state? *Geophys. Res. Lett.* **30**, 1992. (doi:10.1029/2003GL018126)
- 35 Dlugokencky, E. J., Masarie, K. A., Lang, P. M., Tans, P. P., Steele, L. P. & Nisbet, E. G. 1994 A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992. *Geophys. Res. Lett.* **21**, 45–48. (doi:10.1029/93GL03070)
- 36 Dlugokencky, E. J., Dutton, E. G., Novelli, P. C., Tans, P. P., Masarie, K. A., Lantz, K. O. & Madronich, S. 1996 Changes in CH<sub>4</sub> and CO growth rates after the eruption of Mt. Pinatubo and their link with changes in tropical tropospheric UV flux. *Geophys. Res. Lett.* **23**, 2761–2764. (doi:10.1029/96GL02638)
- 37 Dlugokencky, E. J., Walter, B. P., Masarie, K. A., Lang, P. M. & Kasischke, E. S. 2001 Measurements of an anomalous global methane increase during 1998. *Geophys. Res. Lett.* **28**, 499–502. (doi:10.1029/2000GL012119)
- 38 Rigby, M. *et al.* 2008 Renewed growth of atmospheric methane. *Geophys. Res. Lett.* **35**, L22805. (doi:10.1029/2008GL036037)

- 39 Fisher, R. E. *et al.* In preparation. Arctic methane sources: isotopic evidence for atmospheric inputs.
- 40 Fung, I., John, J., Lerner, J., Matthews, E., Prather, M., Steele, L. P. & Fraser, P. J. 1991 Three-dimensional model synthesis of the global methane cycle. *J. Geophys. Res.* **96**, 13 033–13 065. (doi:10.1029/91JD01247)
- 41 Bergamaschi, P., Krol, M., Dentener, F., Vermeulen, A., Meinhardt, F., Graul, R., Ramonet, M., Peters, W. & Dlugokencky, E. J. 2005 Inverse modelling of national and European CH<sub>4</sub> emissions using the atmospheric zoom model TM5. *Atmos. Chem. Phys. Discuss.* **5**, 1007–1066. (doi:10.5194/acp-5-2431-2005)
- 42 Bergamaschi, P. *et al.* 2010 Inverse modeling of European CH<sub>4</sub> emissions 2001–2006. *J. Geophys. Res.* **115**, D22309. (doi:10.1029/2010JD014180)
- 43 Kort, E. A. *et al.* 2008 Emissions of CH<sub>4</sub> and N<sub>2</sub>O over the United States and Canada based on a receptor-oriented modeling framework and COBRA-NA atmospheric observations. *Geophys. Res. Lett.* **35**, L18808. (doi:10.1029/2008GL034031)