DOE Final Report:

Closing the Gaps in The Budgets of Methane and Nitrous Oxide

Principal Investigators: **M.A.K.Khalil, A. Rice and R.A. Rasmussen**
Participating Research Scientists: **M.J.Shearer, C.I. Butenhoff and Z. Xiong**

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1. Introduction

Together methane and nitrous oxide contribute almost 40% of the estimated increase in radiative forcing caused by the buildup of greenhouse gases during the last 250 years (IPCC, 2007). These increases are attributed to human activities. Since the emissions of these gases are from biogenic sources and closely associated with living things in the major terrestrial ecosystems of the world, climate change is expected to cause feedbacks that may further increase emissions even from systems normally classified as natural. Our results support the idea that while past increases of methane were driven by direct emissions from human activities, some of these have reached their limits and that the future of methane changes may be determined by feedbacks from warming temperatures. The greatly increased current focus on the arctic and the fate of the carbon frozen in its permafrost is an example of such a feedback that could exceed the direct increases caused by future human activities (Zimov et al. 2006). Our research was aimed at three broad areas to address open questions about the global budgets of methane and nitrous oxide. These areas of inquiry were: The processes by which methane and nitrous oxide are emitted, new sources such as trees and plants, and integration of results to refine the global budgets both at present and of the past decades. For the process studies the main research was to quantify the effect of changes in the ambient temperature on the emissions of methane and nitrous oxide from rice agriculture. Additionally, the emissions of methane and nitrous oxide under present conditions were estimated using the experimental data on how fertilizer applications and water management affect emissions. Rice was chosen for detailed study because it is a prototype system of the wider terrestrial source, its role in methane emissions is well established, it is easy to cultivate and it represents a major anthropogenic source. Here we will discuss the highlights of the results that were obtained.

2. Q10's Of Emissions

2a. Theoretical Framework:

We have isolated six processes that constitute methane emissions from terrestrial ecosystems including wetlands, plants and rice fields. Of these, four are related to transport, and the other two are production and oxidation. The transport processes take methane from the anoxic levels of soils to the root zone, from the root into the plant, from the plant into the atmosphere and the fourth is a direct path from the soil to the air bypassing the plant, as may occur when bubbles rise to the surface from inundated land. A minimalist model of these processes results in the following relationship between the emissions or flux and the underlying processes (see Fig 1):

$$F = \frac{P\delta_s}{1 + \frac{\tau_T}{\tau_o}} \qquad (1)$$

Where F is the flux of methane (in mg/m^2- h), P is the rate of production of methane (in mg/m^3-h), δ_s (m) is the depth of active soil and the τ's are the transport (T) and oxidation (O) times.

<> <> Fig 1 <> <>

It is apparent that the change of flux with temperature will depend on how each of these processes changes as the temperature increases. If increase of flux can be represented by an exponential function of temperature, as is usually assumed, then the Q_{10} is represented by the following formula:

$$Q_{10} = \left[\frac{F(T+\Delta)}{F(T)}\right]^{10/\Delta} \qquad (2)$$

Where F(T+Δ) and F(T) are the fluxes at temperatures T and T+Δ, measured or calculated.

Making the assumption that each of these processes increases exponentially with temperature leads to the following relationship between the Q_{10} of the flux and the Q_{10}'s of the individual processes:

$$Q_{10}(F) = Q_{10}(P)\left[\frac{Q_{10}(T)}{Q_{10}(O)}\right]^{\left(\frac{R_0}{1+R_0}\right)} \qquad (3)$$

Where R_0 is the ratio of the transport over oxidation times at the base temperature T_0, and the symbols F, P, T and O are flux, production, transport and oxidation respectively. If the oxidation is fast compared with transport, the term in the power approaches 1 and $Q_{10}(F) \approx Q_{10}(P)$ $Q_{10}(T)/Q_{10}(O)$. If, in the other extreme, the transport is much faster than oxidation, the power is 0 and the Q_{10} (F) ≈ Q_{10} (P).

The main point to note is that the Q_{10} of oxidation can offset the increases caused by transport or production. While this is intuitively obvious, the equation above, or a more complex version of the theory allows us to evaluate quantitatively how the final emissions will respond once we understand how the component processes will behave. One set of our experiments were designed to systematically study the Q_{10}'s of the individual processes so that we could better understand how the flux of methane would be affected by climate change.

2b. Q_{10}'s For Rice as a Prototype System:

The experiments used a water bath into which four tubs were placed with the rice plants that were grown under controlled conditions of a research greenhouse. Three were replicates and one was a control with no plants. Each water bath was kept at a different temperature. The temperatures chosen were: 20, 24, 28 and 32 ºC representing approximate current conditions as well as warmer and cooler situations. From these experiments the Q_{10} of the flux could be determined directly. Soil core samples taken at regular intervals were incubated to see how the methanogenic bacteria that were making the methane in these systems reacted to the different temperatures resulting in a measure of the Q_{10} of the production. Additionally the measurement of mcrA and pmoA gene copies gave us an estimate of the populations for methanogens and methanotrophs respectively. This provides another measure of the Q_{10} of production and also a measure of the Q_{10} of oxidation. An alternative isotope method for measuring the Q_{10} of oxidation was also used giving an independent estimate that is consistent with the values reported here. The Q_{10} of transport was not directly measured in these experiments, however, it was calculated from Eqn. 3 since all other terms were measured. In another set of experiments done to evaluate methane emissions from trees and plants the transport Q_{10} was measured and found to be very close to the estimate for rice plants. We show the results that quantitatively summarize the findings Table 1. A re-analysis of long-term data from earlier field experiments at Tu Zu and Jin Sa in Sichuan China are shown in Fig. 2. (Khalil et al. 2008; Sithole, 2011; Sithole et al. 2013; Khalil et al. 2013)

<> <> Table 1 <> <>
<> <> Figure 2 <> <>

The results in Fig 2 are a unique time series of Q_{10}'s of the flux from field experiments. These are based on thousands of flux experiments under field conditions that are not as controlled as in the greenhouse. The results are remarkably consistent with the greenhouse data on the flux Q_{10}'s. Moreover, we see that there is an inter-annual variability including one year where there was no response. We attribute these changes to the relative variation of oxidation and production processes from year to year. We note that the oxidation Q_{10} is considerably larger than the response of production and transport. Oxidation can therefore pull the flux Q_{10} below 1, that is produce a net negative feedback under the right circumstances. It will also keep the Q_{10} of the flux lower than what would be expected from the response of production and transport.

The results in Table 1 are being verified and should be considered tentative, however, if they stand, oxidation may be regarded as the controlling variable for the future feedbacks from the type of system we have studied because it has a greater response to temperature change. The feedback from temperature change may be positive in some areas such as wetlands and rice where production is greater than oxidation and negative in others such as under dryer conditions when the production is less than oxidation. The dry or moist soils are generally a net sink of methane which is estimated to be ~ 50 Tg/y; that sink may increase with warming.

2c. *Nitrous Oxide Experiments.*

In most experiments, nitrous oxide was measured at the same time as methane. Some modification of sampling strategies was needed to capture the flux of nitrous oxide, however, the results are not definitive since the processes controlling the emissions could not be isolated in these experiments.

The typical pattern of nitrous oxide emissions from inundated systems represented by rice is that the largest emissions occur soon after application of nitrogen based fertilizers and persist for a few days to a week. After that, the emissions do not occur or are sporadic and small. In Fig 3 the emissions for two weeks following fertilizer application are shown in contrast to emissions for the rest of the season that lasted another 143 days. From the greenhouse measurements taken at the same time as methane, the Q_{10} in the early phase after fertilizer was applied was 1.9 but after that there was no statistically significant net temperature response and the Q_{10} was about 0.7 with large uncertainties (see Fig 3).

<> <> Figure 3 <> <>

3. Transport Processes in Plants and the Temperature Response.

The general process that controls emissions from rice and wetlands is likely to occur elsewhere when vegetation is present. The reasoning is that the root exudates, dying roots, litter and other dynamic processes of vegetated areas would provide the substrates to sustain methanogenic bacteria and the buildup of methane below the root zones would lead to transport towards the atmosphere through the soil and roots where oxidation will occur. If trees and shrubs were efficient at transporting this methane then a flux would be observed. Even if it is small, the areal extent of vegetation is so large that it could be a significant global source.

Experiments were conducted to isolate the effect of transport on the flux of methane from plants. The goal was to quantify the speed of this transport as well as the changes that may be expected when the earth warms. In these experiments trees were grown hydroponically in the research greenhouse. A large amount of methane was bubbled into water inside the chamber where the plant roots were then placed. The flux was measured for a day or more afterwards. This eliminates the complex effects of biological and chemical processes in soils and reveals only the role of plant transport processes in the emissions of methane. Further, where the methane came out of the plants was also studied.

These experiments showed several remarkable results. First, the transport processes are slow leading to a half life of about 10 days. Second, a sizable amount of methane appeared to be held in the tree without being released. Third, the Q_{10} of transport was found to be about 2.4 (2.0-3.0) which is similar to the results from the rice experiments. And finally, that most of the methane came out of the stems rather than the leaves (Kutschera, 2013; Kutschera et al. 2013). These findings have significant implications for tree emissions on a global scale. The fact that emissions were seen to come from the stems suggests that transpiration does not play an important role and that methane is prevented from entering the roots. This was further supported by the observation that the emissions were much less than would be dissolved in the transpired water. Because the transport is so slow, according to Eqn 3, we expect that oxidation will remove most of the methane that is produced before it can come out into the atmosphere, thus cycling the carbon in the system as CO2 rather than emitting it as methane. Plants and trees, therefore do not appear to be major sources of global methane.

4. Inverse Model Results: Rice Emission Trends

As part of a larger effort to understand how the global methane budget has been changing over past decades, we estimated global methane emissions over the time period 1985 to 2008 using GLOBALVIEW methane concentrations and dual methane isotopes, $^{13}CH_4$ and CH_3D. We employed a Bayesian estimation technique and a Kalman fixed-lag smoother to invert the methane and isotopic records. We divided global sources into ten categories: gas and oil, coal, livestock, waste, rice, C3-biomass burning, C4-biomass burning, wetlands (30N-90N), wetlands (0-30N), and wetlands (90S-0). Estimates of flux strength for each source on a monthly basis were obtained from the inversion. In addition to our "base inversion" we also performed 42 sensitivity experiments that quantified the sensitivity of the inverted emissions to variables such as model parameters and inputs, uncertainties, and inversion setup, to determine the robustness of the optimized budget and trends. The optimized budget is shown in Table 2 along with the prior source strengths and ensemble spread that includes all 42 sensitivity experiments. The time series of inverted emissions are shown in Figures 4 and 5.

We summarize some of the major findings. For the past two-and-a-half decades there has been little to no trend in total methane emissions, despite inter-annual variability on the order of 40 Tg yr^{-1}. This disagrees with bottom-up inventories that estimate emissions have increased by nearly 80 Tg yr^{-1} since 1985 (EDGAR4). Despite there being no overall trend in the total source strength, we found that this is not the case for individual sources. Rice emissions have decreased by about 10 Tg yr^{-1} since 1985 while emissions from waste and livestock have increased by similar amounts. This is in agreement with our past work and others that indicate rice emissions are decreasing due to changes in irrigation and fertilization practices and livestock emissions are increasing due to increasing livestock populations. The decrease in rice emissions may not be as large as expected from the changes in irrigation and fertilization alone due to offsetting increasing emissions on account of warming temperatures and Q_{10} effects as we discussed above.

Since 2004 the inversion shows that there has been a 20 Tg yr^{-1} increase in emissions from the gas and oil sector. This has been partially offset by a significant decrease in total wetland emissions since the year 2000. Wetland emissions have stabilized since 2005 but are still about 20 Tg yr^{-1} below their 25-year mean. Therefore emissions from both wetlands and rice paddies have decreased in recent years despite warming global temperatures that are expected to increase emissions due to Q_{10} effects. Decreasing wetland emissions may result from a reduction of flooded area that has been observed worldwide (Prigent et al. 2001).

The results are shown in Figs 4 and 5

<> <> Figure 4 <> <>
<> <> Figure 5 <> <>

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Publications and Dissertations Resulting From the Project:

Alec Sithole, 2011 “Feedbacks of Methane and Nitrous Oxide Emissions from Rice Agriculture” PhD dissertation in Applied Physics, Portland State University, Portland, Oregon.

Ellynne Kutschera, 2013 “Mechanisms of Methane Transport Through Trees”, PhD dissertation in Applied Physics, Portland State University, Portland, Oregon.

Florian Roeger, 2013 Inverse Modelling of Global Methane Emissions MS Thesis, Karlsruhe Institute of Technology, Germany, and Portland State University, Portland Oregon.

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Rice, A.L., C.L. Butenhoff, M.J. Shearer, D. Teama, T. Rosensteil and M.A.K. Khalil, 2010. “Emissions of anaerobically produced methane by trees”. *Geophys. Res. Lett*. **37**, doi:10.129/2009GL041565.

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Sithole, A.; Flores, G. E.; Reysenbach, A. L.; Shearer, M. J.; Butenhoff, C. L.; Khalil, A. M., Responses of mcrA and pmoA Gene Copies and Methane Fluxes to Soil Temperature Changes in Rice Microcosms, American Geophysical Union, Fall Meeting 2010, abstract #NS31B-1394

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Methane Emissions From Vegetation:
The Master Mechanism

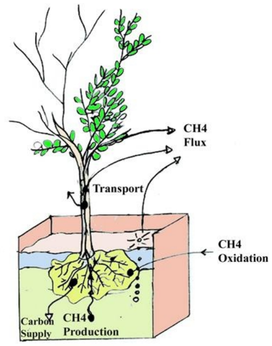


Figure1. A stylized version of the mechanism of methane emissions through plants. Methane is produced in the anoxic soils below, with organic material supplied by the roots. Methane is transported to the atmosphere either through the plant or by bubbles. If it goes through the plant it may encounter oxidizing bacteria in the root zone which consume methane.

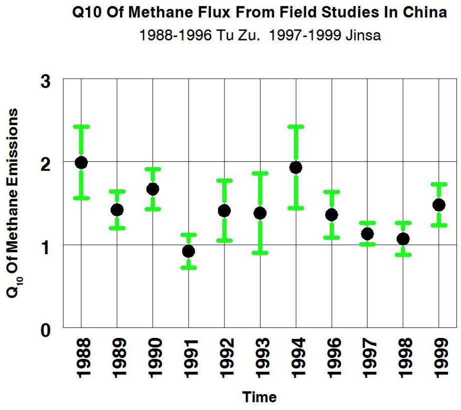


Figure 2. Estimates of Q10 of methane emissions from rice plants based on a longitudinal study spanning eleven years. The inter-annual variability may be caused by the interaction of methane producing and oxidizing processes.

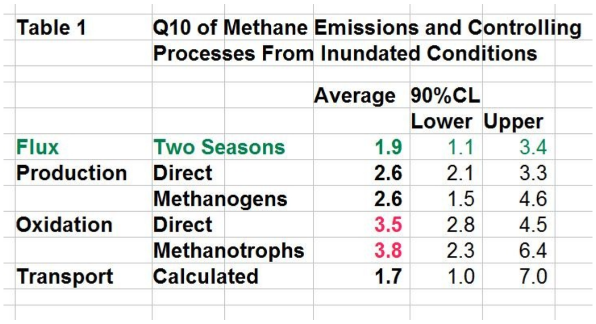


Table 1 **Q10 of Methane Emissions and Controlling Processes From Inundated Conditions**

		Average	90%CL	
			Lower	Upper
Flux	Two Seasons	1.9	1.1	3.4
Production	Direct	2.6	2.1	3.3
	Methanogens	2.6	1.5	4.6
Oxidation	Direct	3.5	2.8	4.5
	Methanotrophs	3.8	2.3	6.4
Transport	Calculated	1.7	1.0	7.0

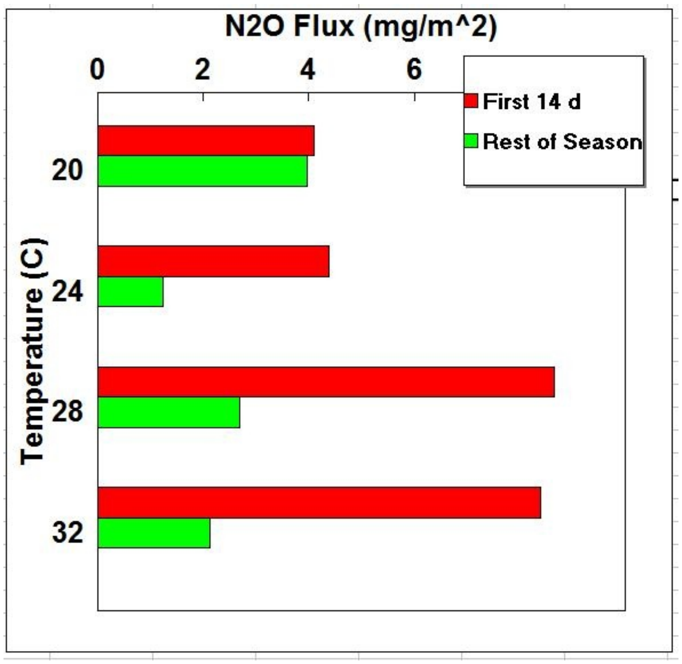


Figure 3: Emissions of nitrous oxide from a rice system at different temperatures. Most of the emissions take place soon after the application of nitrogen fertilizer. In these data, there is no significant temperature response.

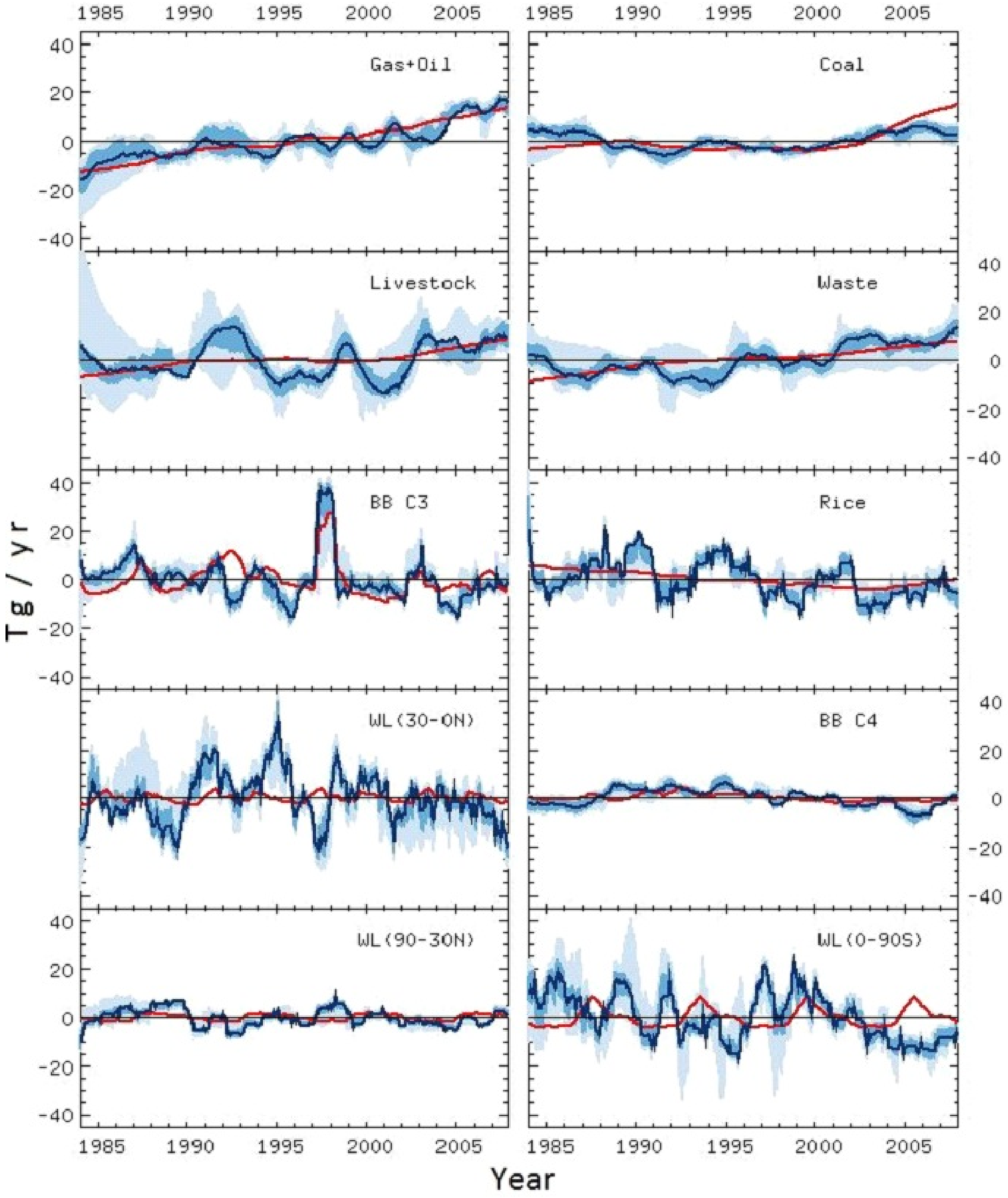
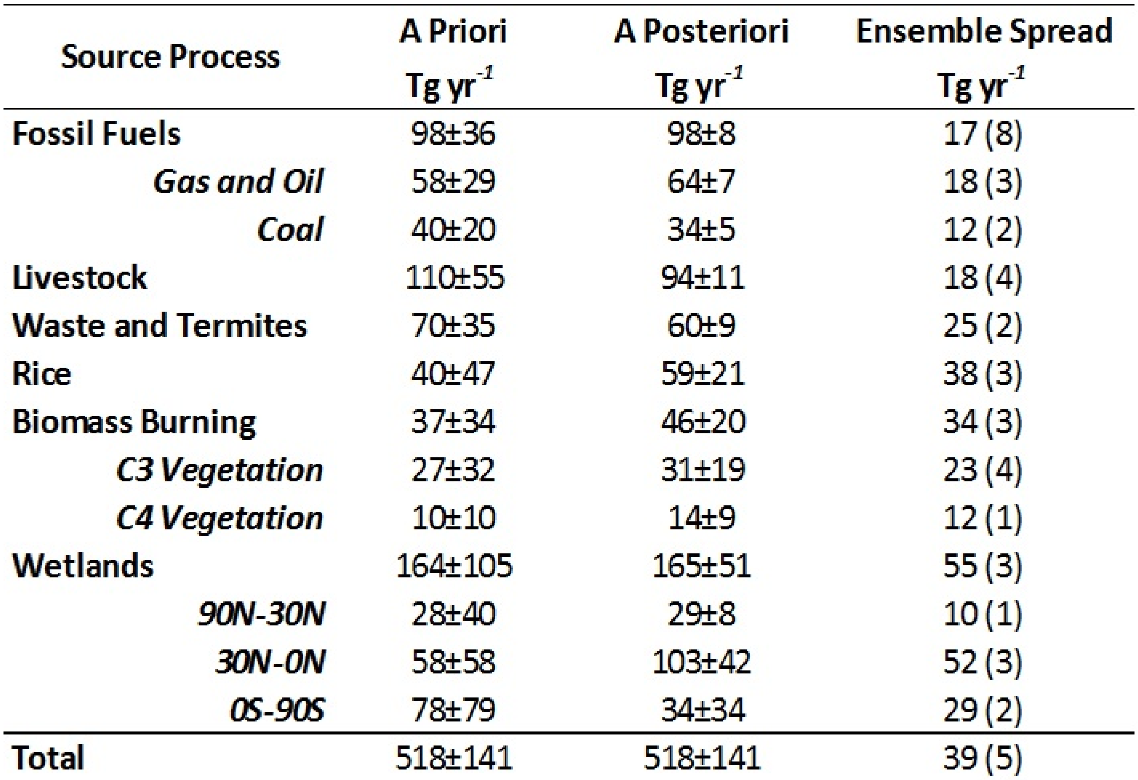


Figure 4: Deseasonalized emission anomalies of all ten basic source categories. The anomalies are calculated by subtracting the long-term means over the whole time period from the deseasonalized (12-months running mean) estimates. Dark blue lines indicate the base inversion. Shaded areas represent the full range of the ensemble (light) and 90% of all estimates (dark). Red lines indicate the anomalies in the priors

Table 2: Comparison of a priori and a posteriori mean methane source strengths over the time period 1984 - 2007. The errors on the optimized estimates are the inversion calculated standard deviations (internal errors). The ensemble spread is taken as the difference between the largest and smallest estimate of all 42 inversions. The values in parenthesis are the corresponding interquartile ranges, containing 50% of all estimates.



Source Process	A Priori Tg yr^{-1}	A Posteriori Tg yr^{-1}	Ensemble Spread Tg yr^{-1}
Fossil Fuels	98±36	98±8	17 (8)
Gas and Oil	58±29	64±7	18 (3)
Coal	40±20	34±5	12 (2)
Livestock	110±55	94±11	18 (4)
Waste and Termites	70±35	60±9	25 (2)
Rice	40±47	59±21	38 (3)
Biomass Burning	37±34	46±20	34 (3)
C3 Vegetation	27±32	31±19	23 (4)
C4 Vegetation	10±10	14±9	12 (1)
Wetlands	164±105	165±51	55 (3)
90N-30N	28±40	29±8	10 (1)
30N-0N	58±58	103±42	52 (3)
0S-90S	78±79	34±34	29 (2)
Total	518±141	518±141	39 (5)

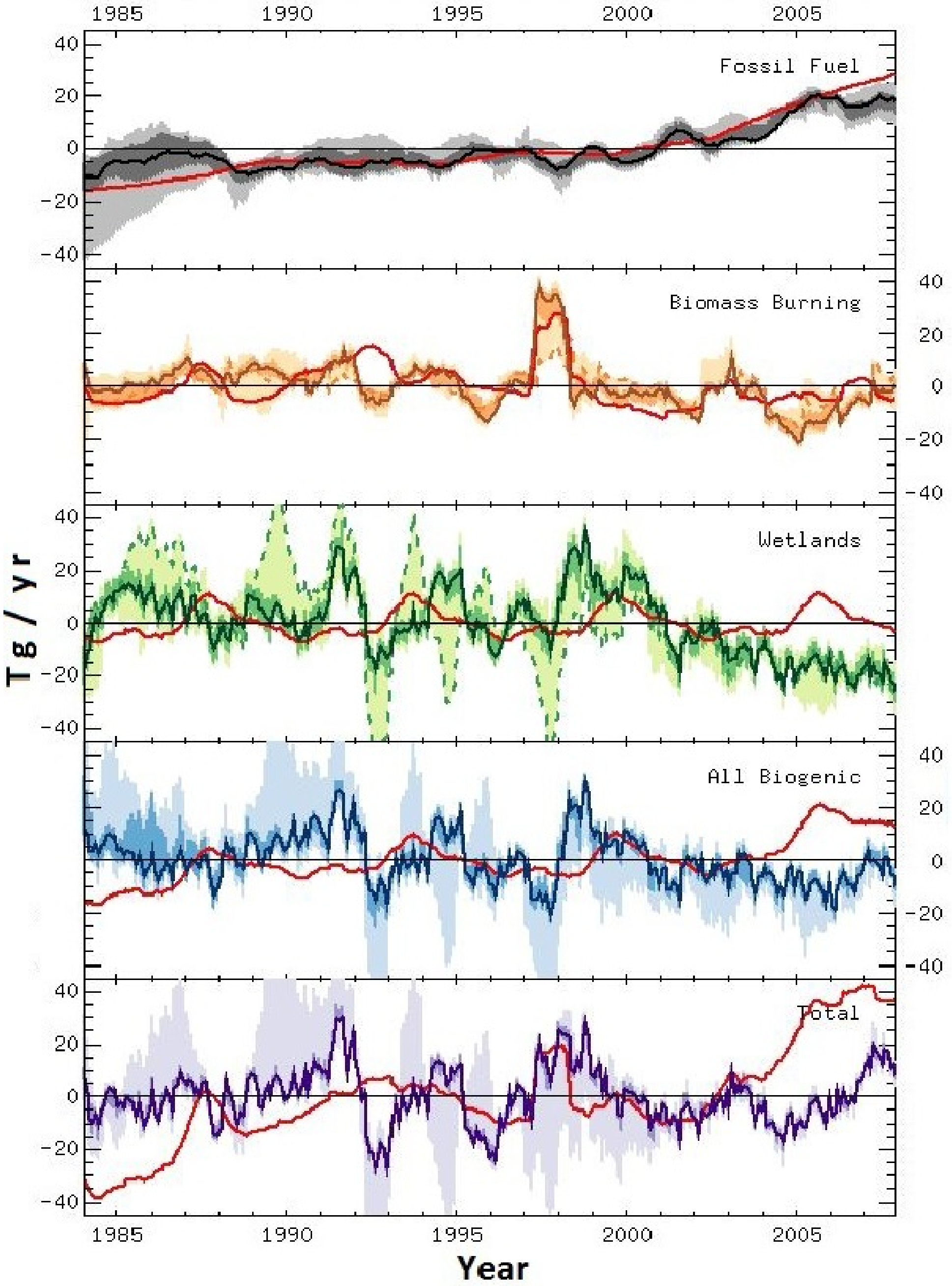


Figure 5: Deseasonalized emission anomalies from aggregated fossil fuel, biomass burning, wetland, all biogenic (including wetlands), and total emissions. Dark colored lines indicate the base inversion. Shaded areas represent the full range of the ensemble (light) and 90% of all estimates (dark). Red lines indicate the anomalies in the priors. The dashed green line indicates wetland emissions in the inversion with inter-annually varying OH and the dashed orange line represents biomass burning emissions in the inversion with uniform observational uncertainties.