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The atmospheric cycling of radiomethane and the "fossil fraction" of the methane source

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Abstract. The cycling of $^{14}CH_4$ ("radiomethane") through the atmosphere has been strongly perturbed in the industrial era by the release of ^{14}C-free methane from geologic reservoirs ("fossil methane" emissions), and in the nuclear era, especially since ca 1970, by the direct release of nucleogenic radiomethane from nuclear power facilities. Contemporary measurements of atmospheric radiomethane have been used to estimate the proportion of fossil methane in the global methane source (the "fossil fraction"), but such estimates carry high uncertainty due to the ill-determined nuclear-power source. Guided by a mass-balance formulation in a companion paper, we apply a contemporary time series of atmospheric radiomethane to quantify both the fossil fraction and the strength of the nuclear power source. We deduce that 30.0±2.3% (1 s.d.) of the global methane source for 1986–2000 has fossil origin, a fraction which may include some ^{14}C-depleted refractory carbon such as from aged peat deposits. Since this estimate depends upon the validity of assumptions underlying a linear regression model, it should be seen as providing a plausible re-estimate rather than a definitive revision. Such a fossil fraction would be much larger (by 50%) than is commonly accepted, with implications for inventory compilation. The co-estimated strength of the global nuclear-power source of radiomethane is consistent with values inferred independently from local nuclear facilities.

1 Introduction

Measurement of the ^{14}C content in atmospheric methane became much more feasible with the advent of accelerator mass spectrometry in the 1980s which is less demanding on sample size by 3–4 orders of magnitude than the proportional counting systems that it has largely displaced. This measurement has provided another tool for understanding the global methane cycle because of the discriminative ^{14}C content among methane sources. In particular, methane originating from geologic reservoirs whose carbon has been isolated from the atmosphere for at least tens of millennia is either devoid of ^{14}C or has immeasurably small levels. Such "fossil methane" sources have both natural and anthropogenic origin.

Natural fossil-methane sources include terrestrial and marine gas seeps, geothermal and hydrothermal systems, mud volcanoes, and clathrate destabilization. Their average aggregate emission is generally considered to be small, usually up to $\sim$10 Tg yr^{-1} (e.g. Lelieveld et al., 1998; Houweling et al., 2000). However, some well-founded estimates are much larger, $\sim$50 Tg yr^{-1} (Lacroix, 1993; Judd, 2000; Etiope and Klusman, 2002; Etiope, 2004), making such sources much more significant.

Anthropogenic fossil-methane sources include methane ventilated from coal mining operations or otherwise outgassed from coal seams (including from abandoned coal mines), well-head losses from oil and gas mining operations, reticulation losses from natural gas distribution networks, and incomplete combustion of fossil fuels. Peat mining may also release ^{14}C-depleted methane.

Methane emissions from fossil fuel mining are strong targets for emission-abatement measures, not only for the environmental benefit, but also for the economic gain in retaining the methane for use as a fuel. Determining the extent of those emissions is important for developing such measures.

Aggregate fossil methane emissions are usually assessed at about 90–120 Tg yr^{-1}, or about 20% (the "fossil fraction") of the total methane source (e.g. Prather et al., 2001). This estimate is directly attributable to systematic determinations of atmospheric $^{14}CH_4$ ("radiomethane") first reported by Lowe et al. (1988). Such determinations, although painstaking and expensive, enable a top-down estimate of the fossil fraction that is not readily obtainable by alternative measurements.

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Table 1. Estimates of fossil fraction, f, based on measurements of atmospheric radiomethane.

Investigators	Sampling Site	Period	Fossil Fraction
Ehhalt (1974)	miscellaneous	1949–1960	<20%
Lowe et al. (1988)	Baring Head, NZ	1987	32% (>23%)
Wahlen et al. (1989)	Mainly N. America	1987	21±3% (1? s.d.)
Manning et al. (1990)	Baring Head, NZ	1987–1988	24% (17–26%)
Quay et al. (1991)	Olympic Pen., WA	1987–1989	16±12% (2 s.d.)
Quay et al. (1999)	Olympic Pen., WA	1987–1995	18±9% (2 s.d.)
This work	Mainly Baring Head	1986–2000	30.0±2.3% (1 s.d.)

Table 2. Estimates of the "NPR factor", ϕ, characterizing the strength of the nuclear-power source of radiomethane from pressurized water reactors, as compiled by Lassey et al. (2007). Uncertainty estimates are ±1 s.d.

Investigators	Reactor Site	Reactor Design	NPR factor (GBq GW_e^{-1} yr^{-1})
Kunz (1985)	NY, USA	USA	298
Kunz (1985)	NY, USA	USA	179
Veres et al. (1995)	Paks, Hungary	Soviet	540
Eisma et al. (1995)	W. Europe	various	361±69
This work	global	all	286±26

Table 1 reports the fossil fraction estimated this way, including the pioneering estimate by Ehhalt (1974) based on opportunistic pre-1960 measurements. The most recent estimate of 18±9% (Quay et al., 1999) covers a 9-year dataset, 1987–1995. The large uncertainty in this estimate results from a significant source of radiomethane being very poorly quantified: nucleogenic radiomethane sourced and vented from nuclear power facilities (e.g. Kunz, 1985).

In a companion paper, Lassey et al. (2007) analyze the radiomethane cycle and its evolution during the nuclear era, exposing the influence of: (a) "bomb ^{14}C", produced in the atmosphere by nuclear weapons tests, propagating through the biosphere into the radiomethane cycle; (b) "nuclear-power radiomethane" (NPR) generated in the fuel and coolant of nuclear power facilities and vented to the atmosphere; and (c) the fossil fraction of the methane source. The NPR source strength is is parameterized by Lassey et al. (2007) and by others as proportional to the electrical power generated by PWRs (pressurized water reactors), which are the most prolific NPR producers. The constant of proportionality, hereafter termed the "NPR factor" and expressed in GBq($^{14}CH_4$) per GW_e-yr generated by PWRs, has been estimated from radiomethane measurements at or near individual facilities or regional air monitoring. Such estimates vary 3-fold (Table 2).

This paper addresses the simultaneous assessment of the fossil fraction (f) and the NPR factor (ϕ) based on atmospheric radiomethane data since 1986 from both hemispheres. Lassey et al. (2007) show that the growth in NPR, moderated by the superposed tail of the propagating bomb ^{14}C pulse, is the main determinant of the growth in atmospheric radiomethane above a baseline that is largely determined by the mean fossil fraction prevailing over the preceding few years. These distinct roles of f and ϕ permit their simultaneous assessment.

Section 2 summarises from Lassey et al. (2007) the description and related definitions of radiocarbon cycling through the biosphere, particularly the propagation of the bomb ^{14}C pulse. Section 3 presents the mathematical framework that allows the fossil fraction and NPR factor to be evaluated through regression analysis; this section can be skipped by the reader with no interest in that framework. Subsequent sections present and discuss the numerical results and their uncertainties, followed by the conclusions.

2 The role of bomb ^{14}C cycling

Bomb ^{14}C is generated through the reaction of atmospheric ^{14}N with intense neutron fluxes produced by nuclear-weapon detonations in the atmosphere. Such weapon tests were mainly in the late 1950s and early 1960s, with 1962 the single most prolific year. Following the Limited Test Ban Treaty in 1963 only relatively few and isolated tests were conducted by non-signatories France and China (Hua and Barbetti, 2004, Fig. 1). The oxidation product, $^{14}CO_2$, was at its peak abundance in 1964–1965, almost doubling the level of a decade earlier, before declining with the transfer of CO_2 to other carbon pools through photosynthesis and ocean dissolution.

Photosynthetically-fixed carbon is a substrate for methane production, whether by microbial action, through biomass combustion, or via the unknown mechanism of plant-sourced methane recently discovered by Keppler et al. (2006). We refer to the methane so produced as "biospheric methane", and to its radiomethane content as "biospheric radiomethane" (BR). Lassey et al. (2007) model bioshperic carbon dynamics by specifying a distribution of "biospheric lag times", $F(t_{\mathrm{lag}})$, which, without guiding data, they take to be an exponential distribution:

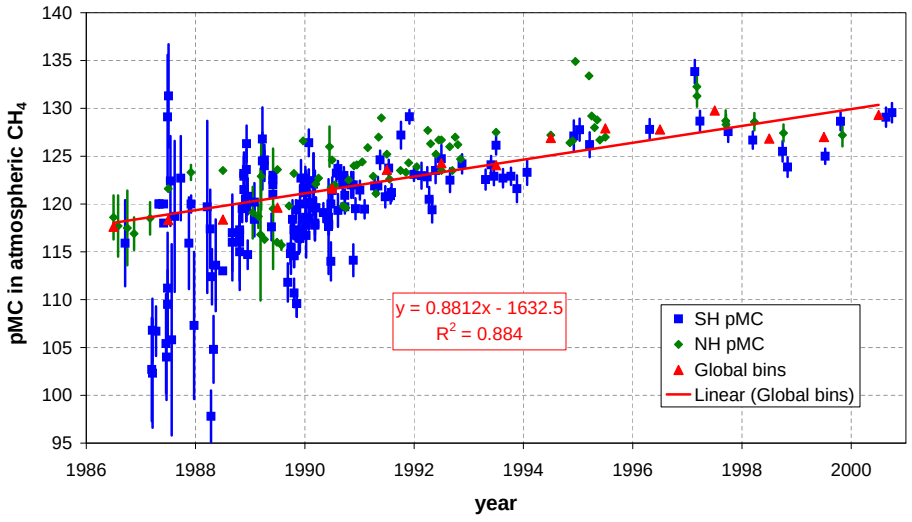

Fig. 1. A scatter-plot of 230 individual $P_A(t)$ measurements (72 and 158 in the Northern and Southern Hemispheres marked green and blue) made by several research groups and kindly supplied for the composite record. Error bars (1 s.d.) are shown where supplied. Also shown is the annualised binned record, the means in each hemisphere in each calendar year averaged over the hemispheres, and the linear regression fit to that binned record with equation and R^2 value. Only the binned means are used in calculations reported in this paper.

$$F(t_{\rm lag}) = \tau_{\rm lag}^{-1} \exp(-t_{\rm lag}/\tau_{\rm lag}) \quad (1)$$

The sole parameter of this distribution, the mean (and standard deviation) lag time $\tau_{\rm lag}$, is optimized by matching simulations to radiomethane data for Antarctic firn air, yielding $\tau_{\rm lag}$=6 years (D. M. Etheridge, personal communication, 2006). The uncertainty in this estimate is difficult to quantify accurately, but is of order ±50%. A Δ^{14}C time series can then be constructed for the global biospheric methane source by convolving Δ^{14}C in atmospheric CO_2, $F(t)$, and radioactive decay (Eq. (6) below). The definition of Δ^{14}C is (Stuiver and Polach, 1977):

$$\Delta^{14}{\rm C} = \frac{A_S}{A_{\rm abs}} \left(\frac{0.975}{1+\delta^{13}{\rm C}} \right)^2 - 1 \quad (2)$$

Here, A_S and $A_{\rm abs}$ are respective activities in the sample corrected for radioactive decay since the date of collection, and in the "absolute international standard" defined for 1950. The accepted value for $A_{\rm abs}$ is 0.2260±0.0012 Bq gC^{-1} (Stuiver, 1980) in which 1 Bq converts to 433.2 fmole(^{14}C).

3 Mathematical framework

We develop a regression approach to calculating simultaneously: (i) the fossil fraction of the methane source, f; and (ii) the NPR factor, ϕ. Each is necessarily averaged over the "regression interval" which is within the period 1986–2000.

The mass balance equations for total methane and for radiomethane are, respectively

$$\dot{C} = S - \lambda C \quad (3)$$

$$\dot{C}_{14} = S_{14} - (\lambda_{14} + \lambda_R) C_{14} \quad (4)$$

in which the overdot signifies time derivative, C and S are the tropospheric burden and source, and λ_R is the radioactive decay constant (8267 yr)$^{-1}$. Methane quantities are expressed in Tg(C), radiomethane in GBq. Tropospheric removal rates of methane and of radiomethane, λ and λ_{14}, are related through mass-dependent isotope fractionation:

$$\lambda_{14}(t) = \alpha^2 \lambda_{12}(t) \approx \alpha^2 \lambda \quad (5)$$

where α=$\lambda_{13}/\lambda_{12}$ is the isotope fractionation factor.

Dependences upon C_{14} and S_{14} can be transformed to dependences upon their respective Δ^{14}C, or more succinctly upon P_A and P_S defined by:

$$P_A(t) = 1 + \Delta_A(t)$$

$$P_S(t) = 1 + \Delta_{BR}(t) = \int_t^\infty \left(1 + \Delta_{\rm CO2}(t-t')\right) F(t') \exp(-\lambda_R t') dt' \quad (6)$$

in which $\Delta_A(t)$, $\Delta_{BR}(t)$, $\Delta_{\rm CO2}(t)$ are the Δ^{14}C time series for atmospheric methane, for the biospheric methane source, and for atmospheric CO_2, respectively. Expressed as percentages, $P_A(t)$ and $P_S(t)$ are the "percent modern carbon" (pMC) time series for atmospheric methane and its biospheric source. From definition (2) can be derived:

$$C_{14} = \kappa_A C P_A \quad (7)$$

$$S_{14} = S_{NPR} + (1-f)\kappa_S S P_S \quad (8)$$

where

$$\kappa_j = \left(\frac{1+\delta^{13}{\rm C}_j}{0.975} \right)^2 A_{\rm abs}, \quad j = A \quad \text{or} \quad S \quad (9)$$

Table 3. The fossil fraction, f, and "NPR factor", ϕ, and their sensitivity to the choice of both the regression interval and the biospheric lag function, Eq. (1). All uncertainties are ±1 s.d. in the regression fit.

Regression Interval	$\tau_{\rm lag}$ (yr)	Fossil Fraction	NPR factor (GBq GW_e^{-1} yr^{-1})
1986–2000	6	30.0±2.3%	286±26
1986–1995	6	29.8±3.2%	283±32
1991–2000	6	29.6±5.1%	284±38
1986–2000	3	26.5±2.4%	276±25
1986–2000	4.5	28.6±2.3%	283±25
1986–2000	9	30.3±2.3%	277±25
1986–2000	12	28.7±2.3%	260±24
1986–2000	n/a[a]	29.2±2.2%	286±25

[a] In place of the distribution of lag times given by Eq. (1), the time lag $t_{\rm lag}$ is taken to be exactly 6 years.

Time dependences are suppressed, and the expression for S_{14} explicitly segregates the NPR and BR sources. Terms $\delta^{13}C_A$ and $\delta^{13}C_S$ denote $\delta^{13}C$ values in the atmosphere and mean source, implying a neglect of variations in $(1+\delta^{13}C)$ among biospheric sources and incurring minor error that we address below. Without such neglect biogenic and pyrogenic contributions to S_{14} would have different weightings, and the source could not be characterized as having merely "fossil" and "non-fossil" components.

Substituting Eqs. (5, 7) into (4) yields

$$S_{14} = \kappa_A \left\{ C P_A(\alpha^2\lambda + \lambda_R) + C\dot{P}_A + \dot{C} P_A \right\}$$

which, through substituting Eq. (3) for $\dot{C}$ can be recast

$$S_{14} = \kappa_A \left\{ S P_A + C\dot{P}_A + C P_A \left(\lambda_R - (1-\alpha^2)\lambda \right) \right\} \quad (10)$$

The first term of Eq. (10) is numerically dominant, accounting for ∼95% of the total in our numerical application of Sect. 4. The third term accounts for ∼1%. We treat $\dot{P}_A$ as constant to be evaluated by regressing $P_A(t)$ on t.

The NPR source is parameterized as

$$S_{NPR}(t) = \phi G(t) \quad (11)$$

in which $G(t)$ is the time series of PWR-generated electrical power (Lassey et al., 2007, Table 3) expressed in GW_e.

Expressions (8) and (10) for S_{14} can be equated, and the result configured as a linear regression problem by defining:

$$X(t) = \kappa_A^{-1} \frac{G}{P_S}$$

$$Y(t) = \frac{P_A}{P_S} + \frac{C\dot{P}_A}{S P_S} + \frac{C P_A}{S P_S} \left(\lambda_R - (1-\alpha^2)\lambda \right) \quad (12)$$

again with time dependences suppressed, so that

$$Y(t) = m X(t) + b \quad (13)$$

in which

$$m = \phi / S \quad \text{and} \quad b = (1-f)\kappa_S / \kappa_A \quad (14)$$

The three contributions in Eq. (12) to $Y(t)$ are those in Eq. (10) to S_{14}: the first term is "numerically dominant", the second "numerically minor", and the third "numerically ignorable". Thus f and ϕ/S are expressed in terms of measurement-based entities together with S in the numerically minor term, and $\tau_{\rm lag}$ through Eqs. (6) and (1).

Provided that there is a large enough spread in $X(t)$ and $Y(t)$ values (i.e. a long enough regression interval), a linear regression of Y on X yields b as the Y-intercept and m as the slope, from which f and ϕ follow by inverting Eqs. (14). An assumption here is that S has not changed systematically over the regression interval, which is consistent with some interpretations of budget changes since ca 1986 (Dlugokencky et al., 1998, 2003; Cunnold et al., 2002). However, a claim of no systematic change in S over 1986–2000 could be questioned (e.g. Dlugokencky et al., 1994; Bousquet et al., 2006), leading us to cross-check using 10-year sub-periods 1986–1995 and 1991–2000 as regression intervals.

Thus m and therefore ϕ are determined by the rate of growth of the PWR industry compared with that of atmospheric radiomethane (taking account of the shape of the tail of the bomb ^{14}C pulse which $\tau_{\rm lag}$ characterizes), while b and thence f are determined by the level of atmospheric radiomethane that is attributable solely to biospheric sources.

4 Results

The fossil fraction f and NPR factor ϕ are evaluated by regression, Eqs. (12–14), over the interval 1986–2000. All contributing terms to $Y(t)$ are included.

The annualized time series $X(t)$ and $Y(t)$ of Eq. (12) are computed using $G(t)$ reported by Lassey et al. (2007, Table 3); $P_A(t)$ is from the annualised series $\Delta_A(t)$ similarly reported (ibid, Fig. 6), as is $\Delta_{CO2}(t)$ (ibid, Fig. 4) which is sourced from Hua and Barbetti (2004), and $C(t)$ (ibid, Fig. 1) sourced from MacFarling Meure et al. (2006). The $P_A(t)$ data comprise bins of data from several investigators that weight each hemisphere equally (noting that 69% of the underlying data is from the Southern Hemisphere, mainly Baring Head, New Zealand), and some statistical consequences are discussed in Sect. 5. Regressing $P_A(t)$ on t yields 0.881±0.089 pMC yr^{-1} (1 s.d.) for the time derivative $\dot{P}_A$, with R^2=0.88 (Fig. 1). This value agrees well with 0.8±0.1 pMC yr^{-1} reported by Quay et al. (1999) for 1987–1995. Other parameter values are taken from Lassey et al. (2007): −47.4±0.4‰ for $\delta^{13}C_A$; 560±40 $Tg(CH_4)\,yr^{-1}$ for S; 0.994 ± 0.002 for α; 8.6±0.5 yr for λ^{-1}. Results reported below are insensitive to variations within these uncertainty ranges.

Figure 2 shows the resulting regression fit of Y on X. The fit is of surprisingly high quality ($R^2 = 0.96$) and yields

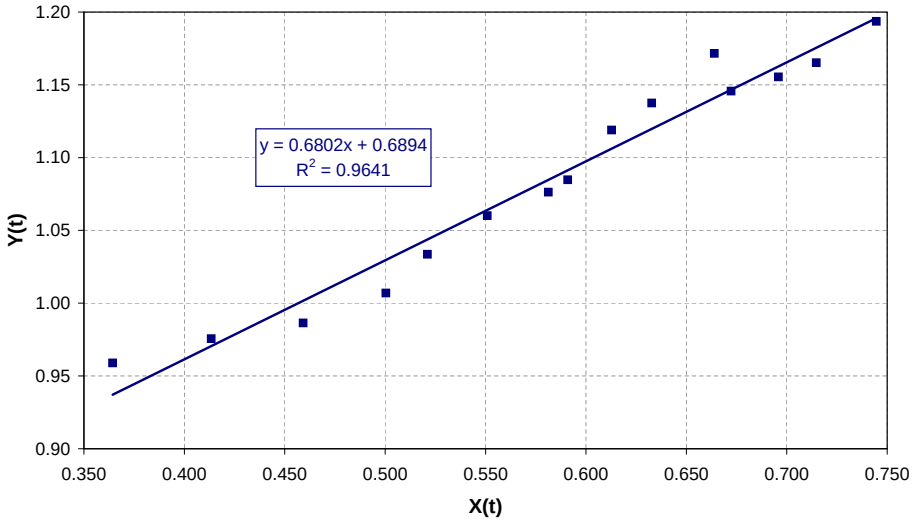

Fig. 2. A plot of $Y(t)$ versus $X(t)$ as defined in Eq. (12) and of the linear regression line of Y on X whose equation and R^2 value are also shown.

slope m=0.680±0.036 GBq GW_e^{-1} $Tg(C)^{-1}$ and intercept b=0.689±0.022 (1 s.d.).

The global $\delta^{13}C_S$ is characterised by −54±5‰ (e.g. Lassey et al., 2007) in which the exaggerated uncertainty (1 s.d.) accounts for variability in $\delta^{13}C$ among individual sources that are predominantly biogenic. The fossil fraction and NPR factor inferred from Eq. (14) are:

$$f = 30.0 \pm 2.3\%, \quad \phi = 286 \pm 26\,\text{GBq}\,(\text{GW}_e\text{-yr})^{-1} \quad (15)$$

The uncertainty (1 s.d.) in f is dominated by that in b with minimal influence from that associated with $\delta^{13}C_S$ which implies that $\delta^{13}C$ variability among biogenic and pyrogenic methane sources is unimportant, while the assumed uncertainty in S (7.1%) is the main determinant of that in ϕ (8.9%).

To test the sensitivity of these results to assumptions, we have performed the following numerical tests, with results reported in Table 3. (i) We restricted to 10-year regression intervals, 1986–1995 and 1991–2000, to test whether any trends emerge. (ii) We applied four τ_{lag} values to distribution (1) roughly reflecting the uncertainty and likely extremes for τ_{lag}. (iii) We simplified the lag distribution of Eq. (1) by taking t_{lag} to be exactly 6 years (equivalent to a "Dirac-δ function" for $F(t_{\text{lag}})$). All R^2 values exceed 0.9 with the smallest values (0.91 and 0.94) for the two 10-year intervals as would be expected.

5 Uncertainties

Confidence intervals reported in Table 3 are "regression errors" (1 s.d.) as they emerge from the linear regression model of Eqs. (12–13) and its underlying assumptions. Errors associated with the validity of that model are necessarily absent. While the high R^2 in the regression fit (Fig. 2) is encouraging, apparently-systematic "wobbles" about the linear fit are unexplained. Moreover, even a slight curvature on the "real" model fit would significantly affect the Y intercept and therefore the inferred fossil fraction, f. In addition, it is worth emphasising that the intercept actually measures $(1-f)$, so that as long as $f<0.5$ the proportional error in f exceeds that in $(1-f)$.

A regression model as applied (for both P_A on t, and Y on X) is based on the assumption that all "measured" values of y for a given x are drawn from a population whose mean is linearly related to x, and additionally whose variance is independent of x. With the latter assumption, errors incurred in measuring y values need not be specified, and the regression analysis estimates the total variance (of both known and unknown origin) based on fluctuations about the linear fit. With each annual bin of $P_A(t)$ data, the underlying confidentially-supplied data have variable and often unspecified quality (Fig. 1). While data in the early part of the record have higher uncertainty, typically 3–5‰ until ca 1988 declining to ∼1‰ in ca 2000 (Fig. 1), this is compensated by a much greater measurement frequency in the earlier period (189 out of 230 included measurements were in 1986–1992). Thus it seems adequate, but not rigorous, to associate a t-independent uncertainty with $P_A(t)$, which Lassey et al. (2000, Fig. 6) assess at ±0.7 pMC, noting that a more complex and subjective weighted least-squares fitting procedure for $\dot{P}_A$ would appear unjustified for a numerically minor term.

A particular vulnerability of this analysis arises if quantities assumed to remain constant during 1986–2000 in fact varied systematically. This includes both f and ϕ (or, strictly, ϕ/S=m) themselves. We tested for such variation by

performing comparative regression fits for each 10-year regression interval 1986–1995 and 1991–2000. While a poorer quality fit (lower R^2) would be expected to accompany the shorter interval, each of the regression-fitted f and ϕ differed insignificantly, both between the two 10-year intervals, and with the common 15-year interval (Table 3). This suggests that systematic changes in the methane budget were either insignificant or unimportant to this analysis. Nevertheless, the constancy of f or ϕ over 15 years could be challenged, and we consider these in turn.

As noted, Dlugokencky et al. (1998, 2003) and Cunnold et al. (2002) report that the secular growth in atmospheric methane in the 1990s was consistent with an unchanging global source (but not necessarily an unchanging geographical distribution). In particular, Cunnold et al. (2002) argue that without changes in the sink strength "emissions were approximately constant ($\pm$20 Tg) from 1985 to 1997 but that in 1997 emissions increased by approximately 37 Tg". This constancy is despite appreciable inter-annual variability throughout the 1990s (Simpson et al., 2002; Bousquet et al., 2006) commencing with a marked decline in atmospheric growth rate in ca 1991 (Dlugokencky et al., 1994). Variations as have been observed have been attributed to effects of the Mt. Pinatubo eruption (in 1991), to climatic effects such as on wetlands (Bousquet et al., 2006), to variations in biomass burning (Simpson et al., 2006), but not to variations in fossil methane emissions.

It could be argued that the global-mean NPR factor ϕ would vary with time in the event that different NPR factors were associated with different reactor designs and that global electricity production by nuclear facilities were generated by a changing mix of designs. In particular, Veres et al. (1995) suggest that Soviet-designed PWRs produce more ^{14}C effluent than western-designed PWRs, as evidenced by measurements near the Paks, Hungary, reactor facility (Table 2), because the use of nitrogen solutes as chemical regulators in the primary coolant allows greater ^{14}C production through the ^{14}N(n, p)^{14}C reaction. However, Lassey et al. (2007) reported that of the electricity production by PWRs, the proportion generated by those of Soviet design did not change significantly over 1986–2000, averaging 14.3$\pm$1.4% (1 s.d.). Consequently, there is no reason to expect a systematic change in ϕ during this interval from a changing PWR mix, unless due to systematic changes in PWR managements or due to influence from non-PWR facilities. Our estimate for ϕ should therefore be associated with an enduring 86:14 mix of electrical power from western:Soviet PWRs.

In addition to vulnerability to systematic variations in f and ϕ, $\dot{P}_A$ is another parameter whose value and constancy could be questioned (Fig. 1), even if it appears only in the numerically minor term of $Y(t)$. All results reported in Table 3 employ $\dot{P}_A$=0.881$\pm$0.089 pMC yr^{-1} as determined by regression of $P_A(t)$ on t over the full 1986–2000 interval. If $\dot{P}_A$ were determined over the same interval as the regression of Y on X, then: (i) for subinterval 1986–1991, $\dot{P}_A$=1.195$\pm$0.082 pMC yr^{-1} and the corresponding f and ϕ are 28.2$\pm$3.3% and 288$\pm$32 GBq (GW$_e$-yr)$^{-1}$; (ii) for subinterval 1995–2000, $\dot{P}_A$=0.564$\pm$0.153 pMC yr^{-1} and the corresponding f and ϕ are 31.1$\pm$5.1% and 278$\pm$38 GBq (GW$_e$-yr)$^{-1}$. This confirms that neither f nor ϕ are sensitive to the particular choice of $\dot{P}_A$, as would be expected from its confinement to a numerically minor term.

Binning the underlying $P_A(t)$ data effectively discards information while reducing the scatter on a plot of $P_A(t)$ versus t. Figure 1 shows the scatter among the underlying 230 data points together with the binned data and its regression fit. The binning process averages all data in each hemisphere in each calendar year and then averages the hemispheres. It is clear that extracting trend information from such scattered data is not unambiguous, and a trend determined through unweighted regression of the binned data is subject to much more uncertainty than is captured in the regression statistics. However, as long as that uncertainty is t-independent, it will contribute uniformly to the error in all $Y(t)$, and therefore not violate the assumption underlying unweighted regression that Y values are drawn from a population with X-independent variance.

In summary, while our regression-based analyses place apparently tight limits on f and ϕ (Table 3) there are unquantifiable errors associated with the validity of the assumptions underlying the linear regression model, for both $P_A(t)$ on t and Y on X. Included in these assumptions are that NPR is emitted "instantly" at a rate $\phi G(t)$ from a PWR industry that is generating electrical power at rate $G(t)$ (an assumption made by all investigators reported in Table 1). Consequences of a poorly-known $\dot{P}_A$ are minimised by its minor numerical importance. Furthermore, $(1-f)$ is inferred from the Y intercept of the Y on X regression line and could be sensitive to any non-linearity, for whatever reason, in the real relationship between Y and X. Thus we believe that our results should be taken to indicate that f could be as high as 30%, which if true would imply a significant adjustment to the global methane budget as currently understood (e.g. Prather et al., 2001).

6 Discussion

A novel approach of this work is in the construction of a Δ^{14}C time series for the global biospheric methane source, $\Delta_{BR}(t)$. Such measurements of Δ_{BR} as have been reported for methane sources have poor global and temporal coverages: most are confined to the late 1980s and early 1990s, and mostly in wetland and rice paddy sources (Lassey et al., 2007, Table 4). We have appealed to the analysis by Lassey et al. (2007) who relate radiomethane content in the global biospheric source to that in atmospheric CO_2 at prior photosynthesis at mean time $\tau_{\rm lag}$ earlier. The latter time series, $\Delta_{CO2}(t)$, is adequately characterized (Hua and Barbetti, 2004; Lassey et al., 2007, Fig. 4). Lassey et al. (2007) show

that τ_{lag} is constrained to about 6 years by Antarctic firn air data dated to the 1970s when the bomb ^{14}C pulse was propagating through the radiomethane cycle. That choice of τ_{lag} does not seem critical to this analysis (Table 3). Thus, in effect, our computational strategy divides the global methane source into two fractions: a fraction $(1-f)$ whose carbon was last photosynthesized 6 years earlier on average; and a fraction f fully devoid of radiomethane. In such a 2-fraction source, f may include refractory carbon such as aged ^{14}C-depleted carbon in peatlands, a possibility that amounts to a conceptual definition of "fossil methane" to include some peat emission. However, such an ambiguity of inclusion cannot be overcome by using poorly representative BR source data to characterize all major biospheric methane sources.

A fossil fraction estimated at 30.0±2.3% for 1986–2000 is quite robust against τ_{lag} at least in the range 4.5–9 years (Table 3), and can be compared with estimates by other researchers within the same time period (Table 1). Lowe et al. (1988) made the first definitive estimate at 32% which Manning et al. (1990) subsequently revised to 24%. Wahlen et al. (1989) incorporated a relatively extensive but localized dataset of $\Delta^{14}C$ from methane sources to estimate the fossil fraction at 21±3%, but with undocumented derivation of uncertainty. The most recent estimate of 18±9% (Quay et al., 1999) used a 9-year dataset of atmospheric radiomethane from Olympic Peninsula, Washington. While the definitions of these various uncertainties are not always clear, the uncertainties themselves are dominated by the uncertain strength of the nuclear-power source. With estimates apparently converging toward about 20%, this value has become viewed as a strong constraint when constructing methane source inventories (e.g. Prather et al., 2001), suggesting a fossil source of ∼90–120 Tg yr^{-1}. The present work is the first attempt to fully utilize data from atmospheric radiomethane monitoring to simultaneously constrain both the fossil fraction and strength of the nuclear-power source, and interestingly favours a value for the former quite close to the original Lowe et al. estimate.

Bottom-up estimates of the anthropogenic fossil-methane emission are generally of similar magnitude to the ∼90–120 Tg yr^{-1} based on a ∼20% fossil fraction (e.g. 92 Tg yr^{-1} for EDGAR 3.2: Olivier and Berdowski, 2001). Such estimates are generally accepted on the basis that natural fossil emissions are minor, typically ∼10 Tg yr^{-1}. However, following Lacroix (1993) and others, Etiope and colleagues (Etiope and Klusman, 2002; Etiope, 2004) contend that natural emissions from geologic formations have been overlooked or under-estimated, and are by themselves in the range 40–60 Tg yr^{-1}, thereby accounting for about half of the global 20%. Thus our estimate of ∼30% for the fossil fraction can accommodate such assessments of geologic methane without compromising present estimates of anthropogenic fossil emission. Indeed it can also accommodate a modest upward revision of the anthropogenic emission to include unaccounted-for sources such as abandoned coal mines (e.g. Kirchgessner et al., 2000).

The estimated NPR factor is within the range of values determined at individual sites (Table 2), and consistent with a top-down estimate for Western Europe (Eisma et al. 1995). It is also consistent with analyses by Lassey et al. (2007) who demonstrate that for a source construction that includes about 21–23% fossil methane (based on EDGAR anthropogenic sources: Olivier and Berdowski, 2001) the value for ϕ of about 190 GBq GW_e^{-1} yr^{-1} that gives the best fit between simulated atmospheric $\Delta^{14}C$ and data is too small for the growth rate in $\Delta^{14}C$ to be fully captured. Lassey et al. argue that a fossil fraction appreciably exceeding 21–23% in tandem with a larger ϕ would improve that simulation.

7 Conclusions

We have calculated simultaneously the fossil fraction f in the global methane source and the source strength of direct radiomethane emissions from global nuclear power facilities. The latter is the "NPR factor", ϕ, which is the radiomethane production per unit of electricity generated from pressurized water reactors. This calculation exploits the fact that the growth in NPR (nuclear power radiomethane) since the 1980s is the principal cause for the growth in atmospheric $\Delta^{14}C(CH_4)$, while the base level in $\Delta^{14}C(CH_4)$ is largely determined by f. This enables both f and ϕ to be determined with greater certainty than determining f alone in the presence of a very uncertain ϕ. Our best estimates during the period 1986–2000, when the character of the methane budget is not believed to have changed markedly (Dlugokencky et al., 2003), are as reported by Eqs. (15), though these estimates do depend upon the validity of assumptions about the quantitative determinants of radiomethane release rates.

Our estimate of f is higher than, though consistent with, the most recent estimate of 18±9% (probably a 95% confidence interval) by Quay et al. (1999). The higher f is also able to accommodate suggestions of a much larger natural geological source of methane than is widely applied to inventories (Lacroix, 1993; Etiope and Klusman, 2002; Etiope, 2004).

Our approach to calculating ϕ arguably provides a superior estimate for radiomethane production by the global PWR industry to those based on individual sites with their individual engineering designs, managements and gas-vent sampling. Our estimate of ϕ is within the range of available estimates (Table 2) that are based on local or regional sampling.

Estimates of both f and ϕ appear robust against variations of the postulated biospheric carbon dynamics (Table 3), and therefore against how the ^{14}C bomb pulse is propagating through the radiomethane cycle.

These results have the potential to modify the present understanding of the methane source inventory. In particular a larger fossil component is suggested which would also result

in a more ^{13}C-enriched source, which in turn has implications for $^{13}CH_4$ balance (Lassey et al., 2007). A larger fossil methane source would also provide impetus for efforts to reduce fugitive methane emissions from coal mining operations and natural gas reticulation if the "extra" methane has a large anthropogenic component, or could stimulate efforts to control or exploit large natural fossil emissions.

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