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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. We exploit an analysis in a companion paper of the global radiomethane budget through the nuclear era, using contemporary measurements of atmospheric radiomethane since 1986 to quantify both the fossil fraction and the strength of the nuclear power source. We deduce that 28.6±1.9% (1 s.d.) of the global methane source has fossil origin, a fraction which may include some ^{14}C-depleted refractory carbon fraction such as in aged peat deposits. 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 in various methane sources. In particular, methane originating from geologic reservoirs whose carbon has been isolated from the atmosphere for tens of millennia is either devoid of ^{14}C or has immeasurably small levels. Such "fossil methane" sources have both natural and anthropogenic origin.

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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 ~10 Tg yr^{-1} (e.g. Lelieveld et al., 1998; Houweling et al., 2000). However, some well-founded estimates are much larger, ~50 Tg yr^{-1} (Lacroix, 1993; Judd, 2000; Etiope and Klusman, 2002; Etiope, 2004), making such sources potentially significant.

Anthropogenic fossil-methane sources include methane ventilated from coal mining operations or otherwise out-gassed 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 of retaining the methane for use as a fuel. Determining the extent of those emissions is important for developing those measures.

Aggregate fossil methane emissions are usually estimated at about 100–120 Tg yr^{-1}, or about 15–20% (the "fossil fraction") of the total methane source (e.g. Prather et al., 2001). This estimate is directly attributable to determinations of atmospheric $^{14}CH_4$ ("radiomethane") pioneered by Lowe et al. (1988). Such determinations, although painstaking and expensive, provide an estimate of the fossil fraction that is not readily accessible by alternative measurements. Table 1 reports the fossil fraction estimated this way. The most recent estimate of 18±9% (Quay et al., 1999) covers a 9-year dataset, 1987–1995. The large uncertainty in this estimate is a result of a significant source of radiomethane being very poorly quantified: the nucleogenic radiomethane sourced and vented from nuclear power facilities (e.g. Kunz, 1985).

In a companion paper, Lassey et al. (2006) analyze the radiomethane cycle and its evolution during the nuclear era, exposing the influence of: (a) "bomb ^{14}C" released in the atmosphere through nuclear weapons testing; (b) "nuclear-power radiomethane" (NPR) generated in the fuel and coolant of nuclear power facilities and vented to the at-

mosphere; and (*c*) the fossil fraction of the methane source. The NPR source strength is poorly quantified, and is parameterized by Lassey et al. (2006) 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, 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 and the NPR factor based on atmospheric radiomethane data since 1986 from both hemispheres. Lassey et al. (2006) show that the growth in NPR 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 permit their simultaneous assessment.

Section 2 summarises from Lassey et al. (2006) 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. Sections 4 and 5 present and discuss the numerical results prior to conclusions in Sect. 6.

2 The role of bomb ^{14}C recycling

Bomb ^{14}C is generated through the reaction of atmospheric ^{14}N with intense neutron beams produced by nuclear-weapon detonations in the atmosphere. Such atmospheric weapons tests were predominately in the late 1950s and early 1960s, with 1962 the single most prolific year. Production ceased with the Limited Test Ban Treaty in 1963 apart from relatively isolated and small tests by non-signatories France and China. The ^{14}C quickly oxidizes to ^{14}CO and within months to $^{14}CO_2$ which participates in photosynthesis and ocean dissolution. The bomb ^{14}C pulse therefore became a valuable

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inadvertent tracer of the global carbon cycle (Nydal and Lövseth, 1983). Following the peak in the tropospheric $^{14}CO_2$ burden in 1964–1965 (at almost double that of a decade earlier), the burden has steadily declined with the net $^{14}CO_2$ transfer to other carbon pools.

The global methane cycle is a minor component of the global carbon cycle. Photosynthetically-fixed carbon is a substrate for methane production, whether by microbial action, through biomass combustion, or through the unknown mechanism of plant-sourced methane recently discovered by Keppler et al. (2006). We refer to the methane so produced as biospheric, and to the radiomethane content as "biosphere-sourced radiomethane" (BSR). Thus the bomb ^{14}C pulse in $^{14}CO_2$ propagated to a delayed and broadened pulse in BSR (Lassey et al., 2006, Fig. 3). Lassey et al. (2006) model the delay as a distribution of lag times, $F(t_{lag})$, and with very little data available, they postulate that an exponential distribution of lag time adequately characterizes all biospheric methane:

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

The single parameter of the distribution, the mean (and standard deviation) lag time τ_{lag}, is optimized by matching simulations to radiomethane data from Antarctic firn air, with a best fit τ_{lag}=6 years (D. M. Etheridge, personal communication, 2006). We apply a simplification of that deduction here: that the $\Delta^{14}C$ value in all biospheric methane sources at time t matches the decay-adjusted $\Delta^{14}C$ value in atmospheric CO_2 at time $(t - \tau_{lag})$, recognising that $\Delta^{14}C$ is preserved between reactant carbon and product carbon by virtue of its definition (2) below. This is valuable because the global $\Delta^{14}C(CO_2)$ time series is much better characterized (e.g. Manning et al., 1990; Levin and Kromer, 2004) than $\Delta^{14}C$ in methane sources, measurements of which are quite sparse both spatially and temporally (Lassey et al., 2006, Table 4). The definition of $\Delta^{14}C$ follows

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Stuiver and Polach (1977):

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

Note that although Δ^{14}C and δ^{13}C values are expressed in "per mil" (‰), the multipliers of 1000 remain implicit and absent from algebraic expressions. A_S and A_{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 (Stuiver and Polach, 1977). The accepted value for A_{abs} is 0.2260±0.0012 Bq/gC (Stuiver, 1980) in which 1 Bq converts to 433.2 fmole(^{14}C).

3 Mathematical framework

We propose a regression approach to calculating simultaneously: (i) the fossil fraction of the methane source, denoted f and expressed numerically in percent; and (ii) the NPR factor, denoted ϕ_{NPR}, which characterizes the strength of the NPR source.

The mass balance equations for total methane and for radiomethane can be cast as

$$\lambda C = S - \dot{C}$$
$$\lambda_{14}C_{14} = S_{14} - \dot{C}_{14} - \lambda_R C_{14} \quad (3)$$

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

$$\lambda_{14}(t) = \alpha^2\lambda_{12}(t) \approx \alpha^2\lambda \quad (4)$$

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

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Equations (3–4) can be combined to remove λ-dependence,

$$\alpha^2 \frac{C_{14}}{C}\left(S - \dot{C}\right) = S_{14} - \dot{C}_{14} - \lambda_R C_{14} \tag{5}$$

Dependences upon C_{14} and S_{14} can be transformed to dependences upon Δ^{14}C. For this purpose, define:

$$\begin{aligned} P_A(t) &= 1 + \Delta_A(t) \\ P_S(t) &= 1 + \Delta_S(t) \approx \left(1 + \Delta_{CO2}(t - \tau_{lag})\right) \exp(-\lambda_R \tau_{lag}) \end{aligned} \tag{6}$$

where $\Delta_A(t)$, $\Delta_S(t)$, $\Delta_{CO2}(t)$ are the Δ^{14}C time series for atmospheric methane, for biospheric methane sources, and for atmospheric CO_2, respectively. $P_A(t)$ and $P_S(t)$ are in fact the "percent modern carbon" values for atmospheric methane and its biospheric source, expressed algebraically as fractions. From definition (2) can be derived:

$$\begin{aligned} C_{14} &= \kappa_A C P_A \\ S_{14} &= S_{NPR} + (1 - f)\kappa_S S P_S \end{aligned} \tag{7}$$

where

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

Time dependences are suppressed, and the expression for S_{14} explicitly segregates the NPR and BSR sources. $\delta^{13}C_A$ and $\delta^{13}C_S$ denote δ^{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} in Eq. (7) would have different weightings, and the source could not be characterized as having merely "fossil" and "non-fossil" components.

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Substituting Eq. (7) into (5), including $\dot{C}_{14}=\kappa_A(C\dot{P}_A+\dot{C}P_A)$, yields after rearrangement

$$\kappa_A\left\{\alpha^2 P_A S + \dot{P}_A C + (1-\alpha^2)P_A\dot{C} - \lambda_R P_A C\right\} = S_{NPR} + (1-f)\kappa_S S P_S \tag{8}$$

During the period of interest (post 1986), the methane cycle has been close to steady state (i.e. $\dot{C}\ll S\approx\lambda C$) so that the first term on the left-hand-side of Eq. (8) dominates the other three, and in our numerical case in Sect. 4 accounts for ~95% of the total. The third and fourth terms are very much smaller than the second and can be ignored. We therefore retain the first two terms, replacing C with $S/\lambda=S\tau$ in the smaller second term at minimal error.

The NPR source is parameterized as

$$S_{NPR}(t) = \gamma\phi_{NPR}G(t) \tag{9}$$

in which $G(t)$ is the time series of PWR-generated electric power (Lassey et al., 2006, Table 3), and γ is the conversion factor 433.2 μmole(^{14}C)/GBq. The simplified Eq. (8) then becomes:

$$\kappa_A S\left(\alpha^2 P_A(t) + \dot{P}_A\tau\right) = \gamma\phi_{NPR}G(t) + (1-f)\kappa_S S P_S(t) \tag{10}$$

The unknowns ϕ_{NPR} and f are thereby expressed in terms of measurement-based entities together with τ, present only in a numerically minor term, and S. It is possible to configure Eq. (10) into a linear regression problem by defining:

$$X(t) = \frac{\gamma}{\kappa_A}\frac{G(t)}{P_S(t)}$$

$$Y(t) = \frac{\alpha^2 P_A(t) + \dot{P}_A\tau}{P_S(t)} \tag{11}$$

so that

$$Y(t) = mX(t) + b \tag{12}$$

in which

$$m = \phi_{NPR}/S \quad \text{and} \quad b = (1 - f)\kappa_S / \kappa_A \tag{13}$$

Provided that there is a large enough spread in $X(t)$ and $Y(t)$ values (i.e., a large enough range of t), a linear regression of Y on X would yield b as the Y-intercept and m as the slope, from which f and ϕ_{NPR} follow by inverting Eq. (13). An assumption here is that S (as well as τ) has no systematic time dependence, which is consistent with the present understanding that S has varied little since the mid 1980s (Dlugokencky et al., 1998, 2003). Thus m and therefore ϕ_{NPR} are determined by the rate of growth of the PWR industry compared with that of atmospheric radiomethane, while b and thence f are determined by the level of atmospheric radiomethane that is attributable solely to biospheric sources.

4 Results

We now pursue a numerical solution to Eqs. (11–13) for the period 1986 to 2000.

The annualized time series $X(t)$ and $Y(t)$ are computed using $G(t)$ reported by Lassey et al. (2006, Table 3), and $P_A(t)$ from the annually-binned series similarly reported (ibid, Fig. 4). While the $P_A(t)$ time series has 2/3 representation from Southern Hemisphere data (mainly from Baring Head, New Zealand), in practice N-S gradients are indiscernible (Quay et al., 1999). The linear trend, $\dot{P}_A$, is computed by regressing $P_A(t)$ on t, which yields the value 0.0792 yr^{-1} (7.92 percent modern carbon per annum) with R^2=0.84. Atmospheric methane is assumed to have δ^{13}C=–47‰ (Quay et al., 1999).

Figure 1 shows the resulting regression fit of Y on X. The fit is of surprisingly high quality (R^2=0.97) and yields m=9.01±0.42 GBq GW_e^{-1} $\mathrm{Tg(C)}^{-1}$ and b=0.704 ± 0.018 (1 s.d.). The fit is insensitive to both α and τ, for which 0.993 and (8.6 yr) are selected.

We characterize the global source by S=560 ± 40 Tg yr^{-1}, and specify $\delta^{13}C_S$=–54±4‰ in which the uncertainty accounts for variability in δ^{13}C among indi-

vidual sources (but a predominance of biogenic sources); both uncertainties are nominally 1 s.d. The inferred fossil fraction and NPR factor are:

$$f = 28.6 \pm 1.9\% \quad \text{and} \quad \phi_{NPR} = 315 \pm 27\, GBq\ (GW_e\text{-}yr)^{-1} \tag{14}$$

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 means that $\delta^{13}C$ variation among biogenic and pyrogenic methane sources are unimportant, while the assumed uncertainty in S (7.1%) is the main determinant of that in ϕ_{NPR} (8.5%).

5 Discussion

A fossil fraction estimated at 28.6±1.9% for 1986–2000 may be compared with estimates by other researchers, all within the same time period (Table 1). Lowe et al. (1988) made the pioneering 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) uses a 9-year dataset of atmospheric radiomethane from Olympic Peninsula, Washington. The definitions of these various uncertainties are not always clear, but appear to be dominated by the uncertain strength of the nuclear-power source. With estimates converging toward 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 ∼100–120 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. It is interesting that the present fossil-fraction estimate not only exceeds the "consensus" value used to constrain the methane source inventory, but is actually closer to the original Lowe et al. estimate.

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A difference between this analysis and those of others is that we do not utilize measurement-based time series of $\Delta^{14}C$ in methane sources. Such source measurements as have been reported 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., 2006, Table 4). In lieu of such time series we have appealed to the analysis of Lassey et al. (2006) who relate radiomethane content in biospheric methane to that in atmospheric CO_2 at prior photosynthesis at mean time τ_{lag} earlier. Lassey et al. (2006) 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). Thus, in effect, our computational strategy divides the global methane sources into two fractions: a fraction (1-f) has a radiomethane content that matches $\Delta^{14}C$ in atmospheric CO_2 6 years earlier; the remaining fraction f is fully devoid of radiomethane. In such a 2-fraction source, f may include refractory carbon such as aged ^{14}C-depleted carbon in wetland peats, a possibility that amounts to a conceptual definition of "fossil methane" that includes some peat emissions. However, such an ambiguity of inclusion cannot be overcome by using poorly representative BSR source data to characterize all major biospheric methane sources.

As noted, hitherto accepted values of the fossil fraction near 20% have been instrumental in constraining the fossil component of the methane source inventory to ~100–120 Tg yr^{-1} (e.g. Prather et al., 2001). Bottom-up estimates of the anthropogenic fossil-methane emission are generally of similar magnitude (e.g. Olivier and Berdowski, 2001), and these 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 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 half of the global 20%. Thus our estimate of 28.6% for the fossil fraction can accommodate such assessments of geologic methane without compromising the 100–120 Tg yr^{-1} of anthropogenic fossil emission.

The estimated NPR factor is within the range of values determined at individual sites

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(Table 2), and fully consistent with estimates by Eisma et al. (1995) for Western European PWRs. Our global constraint on the strength of emissions from the global PWR industry is arguably superior to measurements from individual sites with their individual engineering designs, managements and gas-vent sampling.

6 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_{NPR}, 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_{NPR} to be determined with greater certainty than determining f alone in the presence of a very uncertain ϕ_{NPR}. Our best estimates for the period 1986–2000, when the character of the methane budget is not believed to have changed markedly (Dlugokencky et al., 2003), are f=28.6±1.9% and ϕ_{NPR}=315±27 GBq $(GW_e\text{-yr})^{-1}$ (1 s.d.).

Our estimate of f is higher than, though consistent with, the most recent estimate of 18±9% by Quay et al. (1999). The higher estimate also accommodates suggestions of a higher natural emission of geologic methane than previously adopted widely (Etiope and Klusman, 2002; Etiope, 2004).

Our estimate of ϕ_{NPR} is compatible with the wide range of available estimates (Table 2). In particular, it is consistent with the only other estimate that averages over multiple reactor sites, even if those sites are limited to western Europe (Eisma et al., 1995).

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extracted from air samples at Baring Head, NZ and at Scott Base, Antarctica were analysed for ^{14}C at GNS Science, New Zealand (R. Sparks and colleagues). C. Tuniz (Australian Nuclear Science and Technology Organisation) kindly assembled and supplied data on electricity generation by the nuclear industry while seconded to Australian Permanent Mission to UN organisations and to IAEA in particular. This work was supported by the New Zealand Foundation for Research, Science and Technology under contract C01X0204.

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

Investigators	Sampling Site	Period	Fossil Fraction
Lowe et al. (1988)	Baring Head, NZ	1987	32% (min. 23%)
Wahlen et al. (1989)	Mainly N. America	1987	21±3%
Manning et al. (1990)	Baring Head, NZ	1987–1988	24% (17–26%)
Quay et al. (1991)	Olympic Pen., WA	1987–1989	16±12%
Quay et al. (1999)	Olympic Pen., WA	1987–1995	18±9%
This work	Mainly Baring Head	1986–2000	28.6±1.9%

Table 2. Estimates of the "NPR factor" characterizing the strength of the nuclear-power source of radiomethane from pressurized water reactors, as compiled by Lassey et al. (2006).

Investigators	Reactor Site	Reactor Design	PWR 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	various	315±27

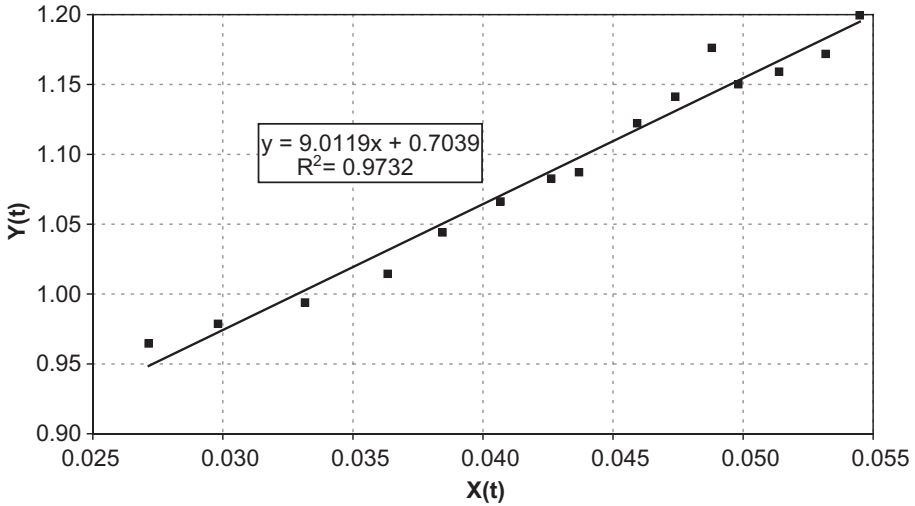

Fig. 1. A plot of $Y(t)$ versus $X(t)$ as defined in Eq. (11) and of the linear regression line of Y on X whose equation and R^2 value are also shown.

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