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QUANTITATIVE DETERMINATION BY ^{14}C ANALYSIS OF THE BIOLOGICAL COMPONENT IN FUELS

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ABSTRACT. Radiocarbon analysis was performed by liquid scintillation counting (LSC) and accelerator mass spectrometry (AMS) to assess whether the content of biological components in hydrocarbon fuels could be derived. Different fuel mixtures were prepared containing bioethanol, fossil ethanol, and fossil gasoline. The specific ^{14}C activity of these mixtures was obtained from LSC measurements and directly related to the concentration of carbon originating from the bioethanol (biocarbon). The results were checked via standardized carbon dating procedures and AMS. A good linear correlation exists between the fuel mixture's specific ^{14}C activity and the concentration of biocarbon. Also, the biocarbon fraction of the fuel mixture (the ratio biocarbon : total carbon) and the normalized fraction of biocarbon (%M) showed good linear correlation. Therefore, both relations provide a possibility to quantitatively determine a fuel's biocarbon content by ^{14}C analysis. When the sample composition is known (e.g. resolved by gas chromatography-mass spectroscopy [GC-MS] and nuclear magnetic resonance [NMR]), the amount of particular biological components in a fuel sample can be derived subsequently. For mixtures of bioethanol, fossil ethanol, and gasoline with bioethanol contents in the range of 0.5–2% m/m, it was found that errors in the normalized fraction of biocarbon (%M) were in the range of 25–10%, respectively. For samples with a higher bioethanol content (up to pure bioethanol), the errors in %M were <10%. Errors might be larger if substantial changes in the concentration of atmospheric ^{14}C took place during the growth period of the biofuel feedstock. By taking into account the variation in specific ^{14}C activity of carbon over the last decades, and by modeling simple tree-growth, it could be illustrated that this effect becomes significant only if the biofuel feedstock stopped growing more than 1 decade ago, e.g. with wood from constructions.

INTRODUCTION

The reliance of present economies on the combustion energy of fossil hydrocarbon fuels has resulted in increased emissions of carbon dioxide (CO_2). Despite uncertainties about the impact of this development on the balance of carbon in the atmosphere, oceans, and land, and ultimately on human beings, much attention currently goes to a reduction of CO_2 emissions (Chase et al. 2001; Alpert et al., forthcoming; Ruddiman 2005; UNFCCC 1997, 2005). In this context, biofuels have been put forward to slow down the growth in CO_2 emissions, particularly from the transportation sector (Cox and Chrisochoïdis 2003). Biofuels can be all fuels of recent biological origin (i.e. produced from biomass), and they are primarily used as a mixture with fossil fuels. Generally, tax measures are applied to achieve a situation in which biofuel prices become comparable with fossil fuel prices (e.g. Brazil, the US, Sweden, France, Germany, Italy). The tax incentives, however, are valid only for the biofuel part. In the Netherlands, an obligation to use biofuels will be enforced beginning in 2007. Thus, it is of interest to be able to differentiate biofuels and fossil fuels (Tamers 2006) and to determine the content of biological components in a fuel. At first glance, this may seem somewhat complicated, because for several biofuels there are fossil counterparts on the market that are chemically identical (see Appendix). Nonetheless, principally it would be possible to overcome this difficulty by analysis of the radionuclide ^{14}C, which is, in contrast to biofuels, practically absent in fossil fuels (Higham 1999; Libby 1952, 1958); this has been demonstrated with natural and synthetic food ingredients (Noakes 1983; Noakes and Hoffman 1980; McWeeny and Bates 1980; Schönhofer 1989; Martin et al. 1981). In the oil industry, however, ^{14}C analysis is not routinely applied. Thus, it is unclear to what concentration level biofuel components can be detected. To get insight into the possibility of using ^{14}C analysis for this purpose, the relation between the biofuel content and the

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^{14}C content was studied using liquid scintillation counting (LSC) and accelerator mass spectrometry (AMS).

METHODS

Compositional data with regard to individual blend components (bioethanol, fossil ethanol, fossil gasoline) and their mixtures (fuel samples) is given below, followed by information on the ^{14}C analysis by LSC and AMS.

Bioethanol

The applied bioethanol (0.7939 g/mL at 15 °C) contains per liter 1.11 g H_2O (KF-titration), <1.0 mg S/kg (UVF), <3.0 mg P/kg (XRF), and 0.3 g of other oxygenates (propanol, 2-methylpropanol, 2-methylbutanol, 3-methylbutanol and traces of 2-butanol, 1,1-diethoxy-2-methylpropane, 3-methylbutylacetate, ethylpentanoate, 1,1-diethoxypentane, ethyl hexanoate) as determined by gas chromatography-mass spectroscopy (GC-MS).

Fossil Ethanol

Compositional analysis of the fossil ethanol (0.7931 g/mL at 15 °C) showed 9.10 mg H_2O/L (KF-titration), <1.0 mg S/kg (UVF), and <3.0 mg P/kg (XRF). In contrast to the bioethanol sample, no organic impurities were found (GC-MS), which is in line with previous observations in the literature (McWeeny and Bates 1980).

Fossil Gasoline

For the sample of oxygenate-free unleaded gasoline ULG95 (0.7547 g/mL at 15 °C), the water and sulfur levels were 25 mg/L (KF-titration) and 42 mg/kg (XRF), respectively. An average molecular formula of $C_{6.53}H_{11.53}$ (89.89 g/mole) was derived from ^{1}H-nuclear magnetic resonance (NMR) and ^{13}C-NMR (using 1,4-dioxane as internal standard, 10% m/m) and GC-MS analysis.

Fuel Samples

Admixtures of oxygenate-free unleaded gasoline (ULG95), bioethanol, and fossil ethanol were prepared with mass ratios as specified in Table 1. The carbon fraction and concentrations are also given, which were derived from the applied quantities of blend components, the purity and the average molecular formula of the blend components, and the sample density.

^{14}C Analysis

LSC was performed at the Wallac Low-Level Laboratory in Turku, Finland, using the Quantulus™ ultra low-level liquid scintillation spectrometer (PerkinElmer 2005). Fuel samples (10 mL) were combined with OptiScint HiSafe (10 mL) and analyzed for 5.5 hr. Channel windows (2.7, 28 keV) were applied to exclude a small contribution from chemiluminescence, which was observed for the gasoline-ethanol mixtures only. (For this purpose, it was also effective to run the experiments with a high bias.) To determine counting efficiencies, i.e. to convert counts per minute (cpm) to decays per minute (dpm), initial measurements were followed by the addition of 100 µL of standard solution containing 2090 dpm of [4-^{14}C]-cholesterol to each sample and a continuation of the analysis for 10 min. To state the results in percent Modern (%M) (Stuiver and Polach 1977), measured specific sample activities were expressed as a percentage of the calculated specific sample activity in the case that all carbon of the sample would be Modern. The sample composition and the 1950 ^{14}C reference specific activity of 13.56 ± 0.70 dpm/g carbon were used (McWeeny and Bates 1980; Ols-

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Table 1 Composition of fuel mixtures, i.e. bioethanol content versus carbon content.

	Mass fractions of blend component (%)			Total carbon concentration	Biocarbon content	
					Concentration	Fraction
Sample	Bioethanol (% m/m)	Fossil ethanol (% m/m)	ULG95 (% m/m)	$C_b + C_f$ [a] (mol/L)	C_b [a] (mol/L)	$C_b/(C_b + C_f)$ [a] (% atom/atom)
1	0.00	0.00	100.0	54.82	0.00	0.00
2	100.0	0.00	0.00	34.39	34.39	100.0
3	0.00	100.0	0.00	34.43	0.00	0.00
4	0.00	10.64	89.36	52.76	0.00	0.00
5	10.01	0.00	89.99	52.88	3.29	6.22
6	5.18	0.00	94.82	53.82	1.70	3.15
7	1.99	0.00	98.01	54.08	0.65	1.20
8	1.02	0.00	98.98	54.27	0.33	0.61
9	0.55	0.00	99.45	54.36	0.18	0.33
10	50.21	49.79	0.00	34.41	17.26	50.16
11	98.05	1.95	0.00	34.39	33.72	98.04
12	99.01	0.99	0.00	34.39	34.05	99.00
13	99.50	0.50	0.00	34.39	34.22	99.50

[a] C_b = carbon from biofuel; C_f = carbon from fossil fuel.

son 1968; Noakes et al., forthcoming). Correction for ^{13}C isotope fractionation was applied by using $\delta^{13}C$ values derived from AMS analysis (see below) (American Society for Testing and Materials 2006; Stuiver and Polach 1977). For the ^{14}C analysis by AMS, fuel samples were catalytically graphitized prior to use. Typically, 2.0 mg of graphitized sample was taken per AMS analysis, which was performed at the Utrecht University AMS facility, the Netherlands. Results are expressed in %M using HOx standards (Stuiver and Polach 1977).

RESULTS AND DISCUSSION

Fuels for combustion engines are generally mixtures of many different hydrocarbons and some oxygenates. Since fuel composition (i.e. the density and the total carbon content) may show a slight variation per batch, the ^{14}C activity of the fuel will not be a direct measure of the biofuel content, but rather of the concentration of carbon that originates from the biofuel components. In other words, ^{14}C analysis of a fuel sample of unknown composition will provide the concentration of biocarbon (or the carbon fraction with a biological origin) and not necessarily the amount of biofuel present in the total mixture. Interestingly, the total carbon content and the fuel composition can be related by standard compositional analysis and density measurements. This is shown in Table 1 for admixtures of oxygenate-free unleaded gasoline (ULG95), bioethanol, and fossil ethanol. With respect to the ^{14}C analysis, bioethanol is considered herein to be representative of all kinds of biofuels containing carbon (see Appendix). To get an indication of a lower detection level, some samples in Table 1 are fossil fuels containing a small quantity of biofuel. Also, the higher levels are of interest because more than 90% of globally produced ethanol is bioethanol (Berg 2004).

^{14}C Analysis Of Gasoline-Ethanol Mixtures by LSC

Initially, the net ^{14}C activity of each gasoline-ethanol mixture was measured with LSC by a direct approach, i.e. without the normalization procedures that are commonly applied in ^{14}C-dating studies

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(Stuiver and Polach 1977). In line with Schönhofer (1989), sample preconversion into CO_2 or benzene was also omitted because no strong LSC quenching effects were observed. The net ^{14}C activities obtained are given in Table 2. For fossil fuel samples with a small content of bioethanol, the error percentages in ^{14}C activity are higher than for bioethanol samples with a small quantity of fossil ethanol. As a result, distinguishing samples 7 and 8 could be achieved but samples 12 and 13 could not (Table 2), although both sets show a difference in ethanol content of 0.50% m/m (Table 1). Nonetheless, an increase in signal-to-noise ratio could be achieved by longer counting times: errors reduced by 29% and 60% at counting times of 11 hr and 34 hr, respectively, i.e. a signal-to-noise ratio proportional to the square root of counting time. Plotting the concentration of biocarbon in the fuel mixtures (C_b) versus the ^{14}C activity and subsequent linear least-squares fitting resulted in a good correlation over a broad composition range (Figure 1). Hence, a calibration plot of C_b versus the net sample ^{14}C activity per unit volume provides the possibility to determine the biocarbon concentration of a fuel by ^{14}C analysis.

Table 2 ^{14}C LSC analysis, 5.5 hr counting.

	Biocarbon content							
	Concentration	Fraction	Net activity			%M [a]		
Sample	C_b [b] (mol/L)	$C_b/(C_b + C_f)$ [b] (% atom/atom)	(Bq/L)	Err.	Err. (%)		Err.	Err. [c] (%)
1	0.00	0.00	0.00	0.12	—	0.00	0.10	—
2	34.39	100.0	100.6	0.81	0.8	108.1	6.25	5.8
3	0.00	0.00	0.00	0.12	—	0.00	0.20	—
4	0.00	0.00	0.00	0.12	—	0.00	0.20	—
5	3.29	6.22	9.32	0.25	2.7	6.53	0.41	6.3
6	1.70	3.15	4.90	0.19	3.8	3.37	0.23	6.8
7	0.65	1.20	1.91	0.18	4.7	1.31	0.14	11
8	0.33	0.61	1.08	0.17	5.3	0.74	0.12	16
9	0.18	0.33	0.79	0.17	5.5	0.54	0.12	22
10	17.26	50.16	51.7	0.58	1.1	55.6	3.24	5.8
11	33.72	98.04	99.2	0.89	0.9	106.5	6.18	5.8
12	34.05	99.00	99.9	0.89	0.9	107.3	6.23	5.8
13	34.22	99.50	100.4	0.89	0.9	107.9	6.26	5.8

[a]Corrected for ^{13}C isotope fractionation ($\delta^{13}C$ data taken from AMS analysis, see text).

[b]C_b = carbon from biofuel, C_f = carbon from fossil fuel. (See Table 1 for the bioethanol content of samples 1–13).

[c]The error in %M differs from the error in ^{14}C activity per liter as a result of the Gauss law of propagation of errors and because of both the spreading of 0.70 dpm/g in the specific ^{14}C activity for carbon and an error of 2.5% in the determination of the carbon content by GC-MS and NMR.

In contrast to the straightforward way of dealing with ^{14}C activity and biocarbon concentration given above, ^{14}C activity in ^{14}C-dating studies is normalized by convention and expressed in percent Modern (%M), i.e. the proportion of ^{14}C atoms in the sample relative to the year 1950 AD (Stuiver and Polach 1977; Higham 1999). This allows interlaboratory comparisons of sample activities (and ages) that are independent of the particular ^{14}C method. Consequently, the results in Table 2 are also given in %M and were derived by using the measured ^{14}C activity, sample composition data, the 1950 ^{14}C reference specific activity of carbon (13.56 ± 0.70 dpm/g) (McWeeny and Bates 1980; Olsson 1968; Noakes et al., forthcoming), and $\delta^{13}C$ data (taken from AMS analysis, Table 3). Notice that with results of ^{14}C analysis expressed in %M, it is not the concentration of biocarbon that will

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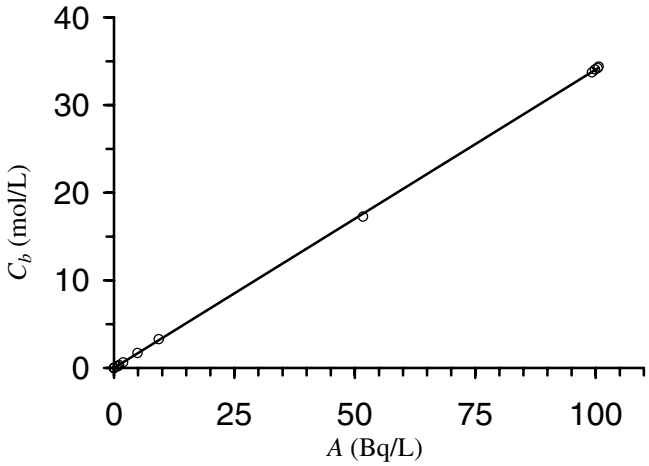

Figure 1 Concentration of biofuel carbon in the fuel sample (C_b) versus specific sample activity (A) by ^{14}C LSC, 5.5 hr counting; linear fit: $C_b = 0.3404 \times A$; $R^2 = 0.9999$.

correlate linearly but the fraction of carbon that is of recent origin, i.e. the ratio biocarbon : total carbon ($C_b/(C_b + C_f)$). This is confirmed by the obtained good linear correlation (Figure 2) and is in line with the result of the first, more direct approach. Hence, by making use of ^{14}C analysis and the type of linear correlations in Figures 1 and 2, it will be possible to determine both the concentration of biocarbon (C_b) and the biocarbon fraction ($C_b/(C_b + C_f)$) for samples of unknown composition. The concentration of biocarbon is, however, something other than the concentration of a particular biofuel component. If the latter is required, then also the molecular formula of the biofuel component has to be determined (e.g. via compositional analysis, see Methods). In the present work, bioethanol is the only biofuel component and, therefore, a separation prior to ^{14}C analysis is not necessary. Thus, how the content of bioethanol relates to the content of biocarbon is established (Table 1). However, if several types of biofuels are part of the total fuel mixture, then separation of the biofuel components may be required prior to ^{14}C analysis (Shibata et al. 2002; Bronk Ramsey et al. 2004; National Diagnostics 2004). In most cases, though, it would be convenient to simply use the total biocarbon content, because it is primarily the replacement of fossil carbon by biocarbon that counts for a reduction in CO_2 emissions.

^{14}C Analysis of Gasoline-Ethanol Samples by AMS

Whereas a ^{14}C atom must disintegrate before it can be detected with LSC, AMS provides direct analysis of ^{14}C atoms. AMS requires smaller sample size and is applied in the present work to verify the %M results from the LSC measurements. With ^{14}C AMS analysis essentially identical, %M results and errors were found (Tables 2 and 3). Consequently, a similar linear correlation between the ratio biocarbon : total carbon ($C_b/(C_b + C_f)$) and the percent Modern (%M) was obtained (slope = 0.9375, $R^2 = 0.9999$ [AMS]; slope = 0.9231, $R^2 = 0.9999$ [LSC]). Hence, the results of the ^{14}C AMS analysis confirm the results of the ^{14}C LSC results.

Contamination with Artificial ^{14}C

Note that the slope of the line that correlates $C_b/(C_b + C_f)$ and %M should not be 0.93 (average of LSC and AMS analyses) but should more closely approximate 1.00. This discrepancy results from

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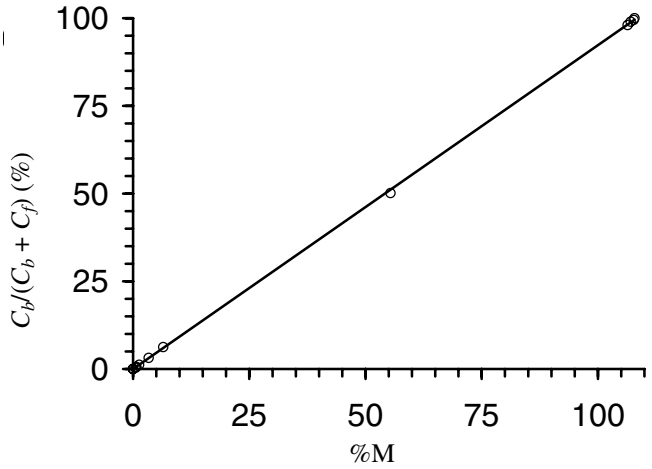

Figure 2 Biofuel carbon : total carbon ratio in the fuel sample ($C_b/(C_b + C_f)$) versus percent Modern (%M) by ^{14}C LSC, 5.5 hr counting; linear fit: $C_b/(C_b + C_f) = 0.9231 \times$ %M, $R^2 = 0.9999$.

Table 3 AMS results of gasoline-ethanol samples.

		%M [a]			
Sample	$C_b/(C_b + C_f)$ [b] (% atom/atom)		Err.	Err. (%)	$\delta^{13}C$ [c] (‰ atom/atom)
4	0.00	0.0	0.1	—	–27.3
5	6.22	6.8	0.1	1.8	–27.1
6	3.15	3.4	0.1	2.9	–27.2
7	1.20	1.2	0.1	8.3	–27.6
8	0.61	0.7	0.1	14	–27.4
9	0.33	0.4	0.1	25	–27.0
11	98.04	103.8	0.5	0.5	–25.6
12	99.00	105.7	0.6	0.6	–26.0
13	99.50	106.8	0.5	0.5	–25.9

[a] Measured percent Modern, normalized to $\delta^{13}C = -25$ ‰ (atom/atom) (Higham 1999).
[b] C_b = carbon from biofuel; C_f = carbon from fossil fuel. (See Table 1 for the bioethanol content of samples 1–13.)
[c] Abundance of ^{13}C relative to ^{12}C with respect to the VPDB reference (Higham 1999).

a variation in specific ^{14}C activity for carbon between 1950 and 2005, which is due to the influx of artificial ^{14}C into the atmosphere as a result of nuclear bomb testing that began after 1950 (McWeeny and Bates 1980; Noakes et al., forthcoming; Rakowski et al. 2005). Hence, if reference is made to the present specific ^{14}C activity for carbon (~14.62 dpm/g; Noakes et al., forthcoming) instead of the conventional reference specific ^{14}C activity for carbon from 1950 (13.56 dpm/g), then a result very close to 1 is found (0.93/[13.56/14.62] = 1.00). Obviously, the accuracy of the ^{14}C determination of the biofuel content is influenced by a variation in specific ^{14}C activity for carbon over time. To estimate the significance of this effect, the following items were taken into account: the decline in specific ^{14}C activity for carbon since 1965 (McWeeny and Bates 1980; Noakes et al., forthcoming; Rakowski et al. 2005); the fact that most recently fixated carbon normally represents

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the highest carbon weight fraction in the sample (during growth, carbon is mainly fixed in a plant's surface layer); and Equation 1:

$$AC_s = \int_{t_s}^{t_e} CWF(t) \times C_s(t) \times dt \quad (1)$$

where AC_s is the average specific ^{14}C activity for carbon in the sample; t is time; t_s is the start of the growth period; t_e is the end of the growth period; $CWF(t)$ is the carbon fixated at time t, expressed as a fraction of the total amount of carbon that is fixated during $t_e - t_s$; and $C_s(t)$ is the specific ^{14}C activity for carbon at time t.

Accordingly, if the bioethanol sample of the present work would have been produced from biomass that was grown and harvested exclusively in 1978 instead of 2003, then the slope of the line that correlates $C_b/(C_b + C_f)$ and %M would have been 0.93/(13.56/18.00) = 1.23 instead of 0.93/(13.56/14.62) = 1.00—a difference of 23%. Alternatively, if the period of growth was 1978–2005, then the average specific ^{14}C activity for carbon in the whole sample would have been 15.27 dpm/g (see Figure 3), resulting in a difference of <5%. Hence, in practice there is a chance of considerable contamination with artificial ^{14}C only if the growth of biofuel feedstock stopped after 1950 and at least a decade ago. Perhaps this is likely for biofuels produced out of used construction wood. For bioethanol, this chance is expected to be small, because for the moment bioethanol is mainly produced from sugar cane, maize, sugar beets, and grapes, or fossil sources.

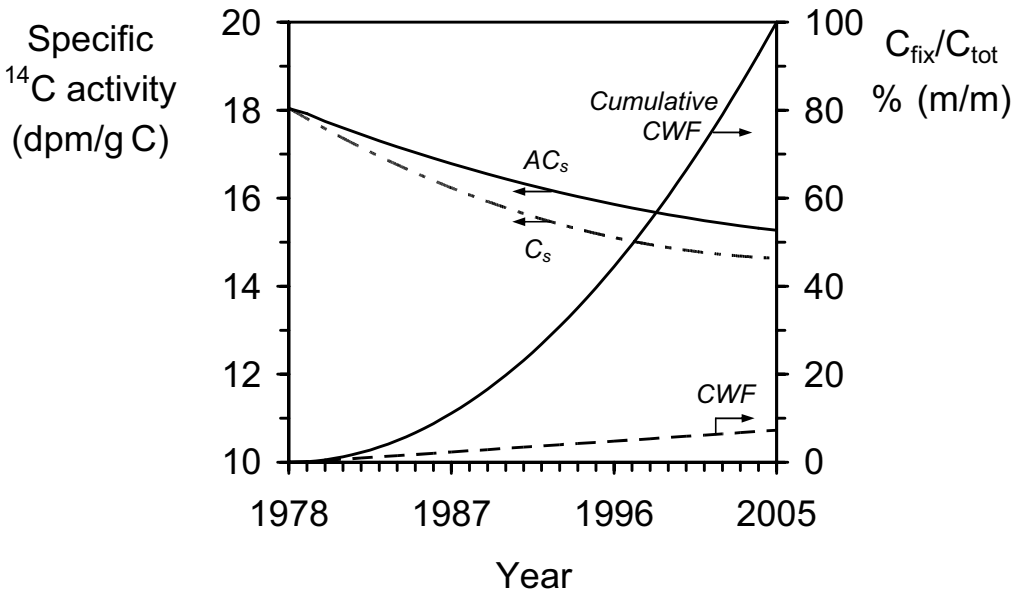

Figure 3 Specific ^{14}C activity of carbon (C_s) during 1978–2005 (McWeeny and Bates 1980; Noakes et al., forthcoming; Rakowski et al. 2005) versus the average specific ^{14}C activity of carbon in a biofuel feedstock sample (AC_s): left axis. The fixation of carbon in biofuel feedstock is indicated as a mass percentage of the total amount of carbon that became fixated during 1978–2005 (*CWF*, *Cumulative CWF*): right axis. The estimation is based on a trunk of a tree that grew during this period, assuming a constant increase of the tree radius.

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CONCLUSIONS

The concentration and fraction of carbon that originates from biological fuel components (biocarbon) shows good correlation with the sample's ^{14}C activity and content, i.e. for admixtures of bioethanol, fossil gasoline, and fossil ethanol. Accordingly, it will be possible to quantitatively determine biocarbon in unknown fuel samples by ^{14}C analysis with LSC or AMS. The content of specific biofuel components can be subsequently determined if the fuel composition is known (determined by GC-MS and NMR). Modeling the growth of biofuel feedstock illustrates that if growth did not stop more than 10 yr ago, then artificial ^{14}C that is in the atmosphere up until today affects the accuracy of the determination of the biocarbon content only to a limited extent.

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APPENDIX

Several biofuels have fossil counterparts that consist of the same molecules. For example, ethanol can be obtained by fermentation of sugars, as well as via hydration of fossil ethene (Logsdon 1994). Another example refers to hydrocarbons that are found in fossil fuels that alternatively can be obtained from a biomass feedstock via hydrocracking or Fischer-Tropsch processes (Boerrigter et al. 2004). Combinations of fossil and biofuels are also conceivable, e.g. blends of fossil and biofuel equivalents. In addition, single components can be partly biological: for example, ethyl tert-butyl ether (ETBE) that is generally obtained as the reaction product of ethanol and fossil isobutene. Another example of this kind is biodiesel that commonly is the ester of vegetable fatty acids and fossil methanol. Finally, biological and fossil equivalents may coexist in exhaust gases when there is a combined use of a fossil and biomass feedstock in a power plant, e.g. as soot particles (carbon), fly ash (traces of carbonate salts), and CO_2 (Shibata et al. 2002; Buchholz et al. 2004; Klinedinst and Currie 1999).