14C CALIBRATION CURVES FOR MODERN PLANT MATERIAL FROM TROPICAL REGIONS OF SOUTH AMERICA

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ABSTRACT. Two $\Delta^{14}C$ calibration curves have been produced that allow determination of the statistical average age of coca leaf and cocaine base specimens produced for the time period 1979–2009. These calibration curves are based on field collections of specimens in Bolivia, Colombia, Ecuador, and Peru. The coca leaf $F^{14}C$ and $\Delta^{14}C$ calibration curves can be used to predict the ages of botanical tissues collected in tropical South America and possibly extended to other tropical locations. The cocaine $F^{14}C$ and $\Delta^{14}C$ calibration curves can be used to predict the ages of seized cocaine specimens. Because the $\Delta^{14}C$ of the atmosphere is diminishing, the precision of this approach for age determinations will continue to get less precise over time as atmospheric ^{14}C content continues to decline.

INTRODUCTION

The decrease in atmospheric $^{14}CO_2$ following the signing of the Nuclear Test Ban Treaty in 1963 has been well described (Levin and Kromer 1997; Hua and Barbetti 2004). Plant archives are commonly used to reconstruct this decline in atmospheric ^{14}C content for dating biological materials in different geographic regions (Hua et al. 2000; McGee et al. 2004). Among the regions less studied for ^{14}C chronologies are tropical regions of the world, where identification of interannual growth represented as tree rings is often hard to detect. Yet, Hua et al. (2000), Lisi et al. (2001), and Soliz-Gamboa et al. (2011) have provided chronologies to show that interannual ^{14}C patterns observed in plants from temperate regions were also detectable and quantifiable in tropical regions as well. However, those records do not extend through the latest time period (i.e. 1990–2009).

Today, bomb dating of modern plant samples is becoming increasingly challenging because the interannual changes in atmospheric $^{14}CO_2$ are far less today than in the 1960s and 1970s (Hua and Barbetti 2007). Small variations in fossil fuel emissions can have a significant impact of quantifying dates for the most recently produced biological tissues, obscuring the vanishing time-stamp ^{14}C signal (Hseuh et al. 2007). Our objective in this study was to develop a high-precision ^{14}C record for the tropical regions of South America that could be used for forensic purposes. Our specific objective was to construct the $\Delta^{14}C$ record for coca leaves (*Erythroxylum coca*) and of the illicit cocaine base extracted from coca. This study builds on initial observations published earlier by Zoppi et al. (2004). Leaves were acquired on specific dates from plantations in Bolivia, Colombia, and Peru. Coca leaves are typically harvested every 3 months, providing a reasonably fine-scale sampling opportunity to construct a $\Delta^{14}C$-time record.

MATERIALS AND METHODS

Coca Leaf and Cocaine Specimen Acquisition

$\Delta^{14}C$ results are reported for 46 coca leaf and 28 cocaine base specimens, obtained through the US Drug Enforcement Administration Special Testing and Research Laboratory (DEA-STRL) in

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Dulles, Virginia, USA, as part of the Cocaine Signature Program (CSP). All coca leaf specimens were acquired in rural regions from plants grown with typical cultivation practices. Site details and specific coordinates are not available. Cocaine specimens included cocaine base specimens obtained using cooks in the field (Casale et al. 2005) and in-country cocaine seizures. Collection dates for coca and cocaine specimens in this study range between early 1980 through mid-year 2009, spanning a Δ^{14}C range of 214‰ to 38‰, respectively. Tables 3 and 4 provide a description of each specimen and its δ^{13}C (‰), F^{14}C, and Δ^{14}C (‰) values, as well as associated analysis errors. All Δ^{14}C data are age-corrected.

Preparation of Graphite Targets for ^{14}C AMS Measurements

Coca leaf and cocaine specimens were each finely ground with a mortar and pestle. A 2-mg subsample was then used for preparing specimens as graphite targets. Determination of Δ^{14}C contents in modern coca leaf and extracted cocaine specimens was made on graphite targets produced from CO_2 that resulted from the combustion of the materials (Xu et al. 2007). The post-2000 specimens were measured on the accelerator mass spectrometer (AMS) at the UC Irvine Keck Carbon Cycle AMS Laboratory (UCI KECK; http://www.ess.uci.edu/ams/). The pre-2000 specimens were measured on the AMS at the Lawrence Livermore National Laboratory Center for Accelerator Mass Spectrometry (LLNL CAMS).

All ^{14}C observations are presented as fraction modern (F^{14}C) or Δ^{14}C (‰) values with units of ‰ or per mil deviation from the 1950 standard (Reimer et al. 2004):

$$F^{14}C = \left[\frac{\left[\frac{^{14}C}{^{12}C}\right]_{sample,-25}}{0.95 \times \left[\frac{^{14}C}{^{12}C}\right]_{Ox1,-19}} \right] \tag{1}$$

$$\Delta^{14}C = \left[\frac{\left[\frac{^{14}C}{^{12}C}\right]_{sample,-25}}{0.95 \times \left[\frac{^{14}C}{^{12}C}\right]_{Ox1,-19} \times \exp((y-1950)/8267)} - 1 \right] \times 1000 \tag{2}$$

where y is the known age of the measured sample.

^{14}C Analysis Precision

Analyses of internal reference materials at UCI KECK allowed us to independently determine the precision of the ^{14}C analyses and, therefore, the age resolution possible for recent coca leaf specimens and/or the cocaine that had been extracted from harvested coca leaves. These reference materials included acetanilide (for use as a blank), oxalic acid (OX2) for data normalization, and ANU sucrose (IAEA C6) and cellulose (IAEA C3) as secondary standards. A second oxalic acid reference material (IAEA C7) was analyzed as an additional quality control measure. The observed Δ^{14}C variations in the reference material over the course of our measurements are summarized in Table 1.

Table 1 Mean ±1 standard deviation (SD) in Δ^{14}C values (‰, measured in 2009) for reference materials from the duration of analysis period.

Reference material[a]	Mean Δ^{14}C ±1 SD	Mean FM ±1 SD	n	Consensus FM
ANU	491.4 ± 2.7	1.5021 ± 0.0027	48	1.5061 ± 0.0011, 1.5016 ± 0.0046[b]
IAEA C3	288.5 ± 4.3	1.2977 ± 0.0043	24	1.2941 ± 0.0006
IAEA C7	−506.8 ± 1.9	0.4967 ± 0.0019	10	0.4953 ± 0.0012
OXII	331.1 ± 2.7	1.3407 ± 0.0028	141	1.3407 ± 0.0019

[a]See IAEA: http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Radionuclides/Carbon14/index.htm.
[b]Consensus data from Xu et al. (2010).

The results in Table 1 show that the ^{14}C dating method resolved differences among any individual sample that were between 1.9‰ and 4.3‰ different in Δ^{14}C. For a coca leaf specimen produced in 2009, this would translate into a resolution estimate for the date for any single observation of 9 months in 2009 and clearly a finer monthly resolution for earlier time periods. In practice, the resolution time of unknown specimens may be greater than this, accounting for calibration, inherent variability in environment, harvest, or processing. In this data set, there are 8 Colombian coca leaf specimens that were harvested and batch processed into cocaine over a 3-day period in 2009. The mean Δ^{14}C ±1σ for coca leaves was 53.2 ± 3.0‰ ($n = 8$; range 49.1‰ to 58.0‰) and for cocaine base, 44.4 ± 3.5‰ ($n = 8$; range 39.6‰ to 49.9‰). This suggests that the mean relative resolution time for an unknown specimen would be similar to what we estimated from our reference materials, about 8 months, but that the range could extend up to 21 months. The biggest error in absolute age of an unknown specimen comes from the uncertainty of the calibration curve, which we expect will improve when additional, high-quality data are available to construct the calibration in the Southern Hemisphere, especially in tropical South America. We calculated ^{14}C analytical precision using IAEA-C3, a secondary reference material, that was analyzed in every wheel with the cocaine and coca leaf specimens. The mean value for IAEA-C3 was Δ^{14}C = 288.5 ± 4.3‰ ($n = 24$, measured in 2009).

Quantifying the Quantities of Solvent Contaminants in Cocaine Specimens

In both controlled laboratory conditions and during clandestine operations, cocaine is extracted from coca leaves through a series of solvent extractions (Casale et al. 2005). Extraction solvents are likely to have been produced through commercial synthetic reactions using syngas and other fossil fuel substrates that do not contain ^{14}C. Solvent residues in the cocaine base would be expected to act as contaminants potentially influencing interpretations of ^{14}C measured on a cocaine specimen. To determine the extent that residual solvent could influence the ^{14}C observations, quantitative qualifications were made of the residual solvent in cocaine specimens (Morello and Meyers 1995; Morello et al. 2000).

Carbon Isotope Ratio Measurement

Carbon isotope ratios (δ^{13}C) were measured on coca leaf and cocaine specimens using an isotope ratio mass spectrometer at the DEA-STRL; the methods were described by Ehleringer et al. (2000). A 2-mg subsample was loaded into a tin capsule in a zero-blank autosampler, interfaced with an elemental analyzer (Carlo Erba), where they were flash-combusted to produce CO_2. The elemental analyzer was coupled to an isotope ratio mass spectrometer (ThermoElectron Delta V) operated in continuous-flow (CF-IRMS) mode. Results for δ^{13}C values are presented on the VPDB scale. The analytical precision (1σ) based on long-term measurements of internal laboratory reference materials for δ^{13}C was ±0.1‰. Stable isotope ratios are reported using the standard δ notation relative to an international standard in units per mil (‰) as $\delta = (R_{sample}/R_{standard} - 1) \times 1000$, where R_{sample} and

$R_{standard}$ are the molar ratios of the heavy to light isotopes of the sample and standard, respectively. Stable isotope ratio data were also measured at LLNL CAMS as part of the ^{14}C measurement process and applied to correct Δ^{14}C to a δ^{13}C value equal to –25‰. At UCI KECK, the on-line AMS δ^{13}C was used for this fractionation correction.

RESULTS AND DISCUSSION

Solvents Are Not a Significant Contaminant Influencing ^{14}C Values

Cocaine base was field extracted from each of 8 batches of coca leaves using traditional illicit methods (Casale et al. 2005). Petroleum-based solvents used in this process contain benzene, toluene, xylenes, and other minor lower boiling petroleum distillates (hereafter referred to as petroleum distillates). The residual trace hydrocarbon solvent concentrations were then measured in each purified cocaine base specimen to determine the potential that residual solvents had influenced the measured Δ^{14}C values (Table 2). We observed extremely low residual solvent levels ($0.0280 \pm 0.0047\%$, mean $\pm$ SD), averaging 0.0089% for xylenes, 0.0083% for toluene, 0.0044% for benzene, and 0.0064% for petroleum distillates. Overall, these solvents contributed a small dead-carbon (no ^{14}C) signal of 0.0235%. Given that there was some small variation in the trace hydrocarbon solvent concentrations among purified cocaine base specimens, we compared individual Δ^{14}C and percent total solvent values for each of the 8 leaf batches. We found no significant correlation between individual Δ^{14}C and percent total trace hydrocarbon solvent values ($r = 0.085$, $p = 0.841$). Based on this low contaminant level and the lack of any significant correlation among residual solvent and Δ^{14}C values, ^{14}C-depleted contaminants were not likely to have contributed any detectable contribution to the measured Δ^{14}C levels in the cocaine specimens.

Table 2 Percentage carbon contributions of the 4 trace solvents (xylene, toluene, petroleum distillates, and benzene) that could contaminate ^{14}C interpretation of a cocaine specimen. "Petroleum distillates" is the sum of the minor low boiling petroleum distillate components. In calculating the percentage dead-carbon contribution, we assume an average C-7 hydrocarbon (83.9% carbon, 16.1% hydrogen).

| Cocaine specimen | Trace solvent, percent contamination (%) | | | | | ^{14}C-dead carbon contribution, % |
	Xylenes	Toluene	Petroleum distillates	Benzene	Total	
N15-P21B	0.0096	0.0088	0.0065	0.0043	0.0292	0.0245
N15-P21D	0.0067	0.0056	0.005	0.0028	0.0201	0.0169
N15-P21F	0.0107	0.0102	0.0073	0.0058	0.034	0.0285
N15-P21H	0.0097	0.0085	0.009	0.0056	0.0328	0.0275
N15-P21J	0.0079	0.0078	0.0057	0.0038	0.0252	0.0211
N15-P21L	0.0082	0.0105	0.0062	0.0064	0.0313	0.0263
N15-P21N	0.0061	0.007	0.0077	0.0037	0.0245	0.0206
N15-P21P	0.0123	0.0078	0.0039	0.0028	0.0268	0.0225
Mean	*0.0089*	*0.0083*	*0.0064*	*0.0044*	*0.028*	*0.0235*

Development of a Coca Leaf ^{14}C Calibration Curve

The Δ^{14}C values of coca leaves harvested from field locations were regressed as a function of the field acquisition date. There was a significant negative, exponential relationship between Δ^{14}C values and year, which explained 93% of the observed variation. This relationship is best described as

$$\Delta^{14}C_{cl} = a \times e^{bT} \tag{3}$$

where $\Delta^{14}C_{cl}$ is the $\Delta^{14}C$ value of coca leaf specimens, $a = 7.8188 \times 10^{48}$, $b = -0.054071$, and T is the time in decimal fractions of the year. Similar observations have been reported previously for the decrease in bomb ^{14}C values. For example, Manning et al. (1990), Nydal and Gislefoss (1996), and Levin and Kromer (1997) reported that the level of bomb ^{14}C decreased exponentially after 1970, halving every 17 yr, 16 yr, and 18 yr, respectively. These values are similar to the 18 yr reported in this study (inverse of decay constant b).

Cocaine is ^{13}C-Depleted and ^{14}C-Depleted Relative to Coca Leaf

The paired $\delta^{13}C$ values of separate batches of coca leaves ($n = 8$) from individual harvests were compared with $\delta^{13}C$ values of cocaine extracted from those leaves. The average $\delta^{13}C$ value of coca leaves (-29.1 ± 0.4‰,) was significantly ^{13}C enriched relative to the cocaine base extracted from these same leaves (-33.6 ± 0.3‰) ($t = 18.49$, $p < 0.0001$, $df = 7$). While the 4.5‰ difference in $\delta^{13}C$ values between coca leaf and extracted cocaine was not surprising, a difference in $\Delta^{14}C$ values between coca leaf and extracted cocaine was unexpected. The $\Delta^{14}C$ values of extracted cocaine base (44.4 ± 3.5‰) were significantly ^{14}C depleted relative to the coca leaves (53.2 ± 2.9‰,) ($t = 5.49$, $p < 0.0009$, $df = 7$). In theory, the $\Delta^{14}C$ values of paired coca leaves and extracted cocaine base should have been the same, as described in Equation 2. However, this was not the observation. It may be coincidental that the 8.8‰ difference in $\Delta^{14}C$ values was almost exactly twice the 4.5‰ difference in $\delta^{13}C$ values. While such a difference might be expected on the basis of ^{13}C versus ^{14}C fractionation differences (Saliege and Fontes 1984), the $\Delta^{14}C$ values of both cocaine base and coca leaf were corrected to a $\delta^{13}C$ value of -25‰ (Equation 2). The basis of the $\Delta^{14}C$ difference between coca leaf and cocaine base remains unexplained, but we can exclude solvent contaminants on the basis of the data presented earlier.

Development of Cocaine $\Delta^{14}C$ and $F^{14}C$ Calibration Curves

All of the available coca leaf and in-country cocaine base seizures were used to construct calibration curves of $\Delta^{14}C$ and fraction modern ($F^{14}C$) in cocaine base versus year. In-country cocaine seizures were assumed to be of the same age as the seizure date, since it is known that the time lag between coca leaf production to cocaine extraction is short relative to the long time lag between leaf production and the appearance of cocaine on the streets in the United States (Ehleringer et al. 2011). Cocaine $\Delta^{14}C$ values were adjusted by 8.8‰ to correct for the observed and unexplained difference in $\Delta^{14}C$ between coca leaf and cocaine base $\Delta^{14}C$ observations (Tables 3 and 4 contain the original data).

The $F^{14}C$ values of cocaine base extracted from coca leaves at field locations (1993–2009) and of in-field seizures of cocaine base (1980–2009) are plotted versus time in Figure 1. An exponential equation explained 96% of the observed variation:

$$F^{14}C_c = d \times e^{fT} \tag{4}$$

where $F^{14}C_c$ is the $F^{14}C$ value of cocaine base, $d = 14776$, $f = -0.0047557$, and T is the time in decimal fractions of the year.

The regression of $\Delta^{14}C$ values of cocaine base extracted from coca leaves at field locations (1993–2009) and of in-field seizures of cocaine base (1980–2009) resulted in an exponential equation that explained 95% of the observed variation. This equation is

$$\Delta^{14}C_c = g \times e^{hT} \tag{5}$$

where $g = 2.7528 \times 10^{42}$ and $h = -0.04661$.

Table 3 For cocaine base specimens seized in the field at various locations in Bolivia, Colombia, Ecuador, and Peru, this is a complete list of the AMS observations and specimen origins. For each specimen, we provide the dates that cocaine base specimens were seized in the field, country of seizure, AMS laboratory conducting the analyses (CAMS = Lawrence Livermore National Laboratory Center for Accelerator Mass Spectrometry; Keck = UC Irvine Keck Facility); carbon isotope ratio ($\delta^{13}C$, ‰), fraction modern ($F^{14}C$) and error, and $\Delta^{14}C$ (‰) and error.

Material	Date acquired	Origin	AMS lab	$\delta^{13}C$ (‰)	$F^{14}C$	$F^{14}C$ error	$\Delta^{14}C$ (‰)	$\Delta^{14}C$ error (‰)
Cocaine base	28 October 1979	Peru	CAMS	−34.5	1.2164	0.0054	211.6	5.4
Cocaine base	28 July 1980	Bolivia	CAMS	−35.0	1.2235	0.0043	218.5	4.3
Cocaine base	1 January 1982	Colombia	CAMS	−35.0	1.199	0.0068	193.8	6.8
Cocaine base	1 December 1983	Peru	CAMS	−34.4	1.1719	0.0041	166.7	4.1
Cocaine base	1 November 1985	Ecuador	CAMS	−35.7	1.1764	0.0041	170.9	4.1
Cocaine base	30 September 1986	Peru	CAMS	−34.9	1.1578	0.0042	152.2	4.2
Cocaine base	4 October 1990	Peru	CAMS	−35.0	1.1541	0.0043	148.0	4.3
Cocaine base	1 June 1993	Bolivia	CAMS	−34.6	1.1274	0.0045	121.0	4.5
Cocaine base	1 June 1993	Bolivia	CAMS	−34.3	1.1418	0.0045	135.3	4.5
Cocaine base	3 October 1993	unknown	CAMS	−35.6	1.1085	0.0039	102.2	3.9
Cocaine base	5 October 1993	Colombia	CAMS	−34.3	1.1106	0.0040	104.8	4.0
Cocaine base	5 September 1993	Colombia	CAMS	−34.3	1.1184	0.0045	112.1	4.5
Cocaine base	1 June 1994	Peru	CAMS	−33.7	1.1203	0.0076	113.8	7.6
Cocaine base	3 January 1994	unknown	CAMS	−35.8	1.1064	0.0039	100.0	3.9
Cocaine base	2 June 1994	Peru	CAMS	−34.8	1.1255	0.0045	119.0	4.5
Cocaine base	2 June 1995	Peru	CAMS	−34.2	1.0935	0.0039	87.0	3.9
Cocaine base	4 March 1998	Bolivia	CAMS	−35.0	1.0924	0.0041	86.1	4.1
Cocaine base	5 November 1998	Colombia	CAMS	−36.0	1.0972	0.0041	90.7	4.1
Cocaine base	6 June 1999	Peru	CAMS	−34.8	1.1011	0.0049	94.6	4.9
Cocaine base	15 May 2008	Colombia	Keck	−33.1	1.0570	0.0030	52.0	3.0
Cocaine base	16 February 2009	Colombia	Keck	−33.6	1.0471	0.0019	39.6	1.9
Cocaine base	16 February 2009	Colombia	Keck	−33.5	1.0475	0.0020	48.4	2.0
Cocaine base	17 February 2009	Colombia	Keck	−33.7	1.0524	0.0019	44.9	1.9
Cocaine base	17 February 2009	Colombia	Keck	−33.6	1.0574	0.0019	49.9	1.9
Cocaine base	17 February 2009	Colombia	Keck	−32.9	1.0496	0.0020	42.1	2.0
Cocaine base	18 February 2009	Colombia	Keck	−34.0	1.0530	0.0022	45.5	2.2
Cocaine base	18 February 2009	Colombia	Keck	−34.0	1.0510	0.0021	43.5	2.1
Cocaine base	18 February 2009	Colombia	Keck	−33.5	1.0487	0.0021	41.2	2.1

Forensic Application of the ^{14}C Cocaine Observation

One application of these $\Delta^{14}C$ observations is determination of the statistical-average age of a seized cocaine specimen, whether it be seized in transit or on the streets in the United States. We calculate the age of a cocaine specimen (T_c) as

$$T_c = \ln(F^{14}C_c/d)/f \tag{6}$$

A second application is to determine the time lag between when a cocaine specimen was grown and the date it was seized. This time lag information might be useful for strategic intelligence and interdiction purposes (Ehleringer et al. 2011). We calculated the expected transit age of a seized cocaine specimen (A_{sc}) in months as

$$A_{sc} = j \times (T_{sc} - T_c) \tag{7}$$

where j is the ratio the number of months (12) to days (365.25) in a year.

Table 4 For coca leaf specimens seized in the field at various locations in Bolivia, Colombia, Ecuador, and Peru, this is a complete list of the AMS observations and specimen origins. For each specimen, we provide the dates that cocaine base specimens were seized in the field, country of seizure, AMS laboratory conducting the analyses (CAMS = Lawrence Livermore National Laboratory Center for Accelerator Mass Spectrometry; Keck = UC Irvine Keck Facility); carbon isotope ratio ($\delta^{13}C$, ‰), fraction modern ($F^{14}C$) and error, and $\Delta^{14}C$ (‰) and error.

| Material	Date acquired	Origin	AMS lab	$\delta^{13}C$ (‰)	$F^{14}C$	$F^{14}C$ error	$\Delta^{14}C$ (‰)	$\Delta^{14}C$ error (‰)
Coca leaf	2 June 1993	Bolivia	CAMS	−29.9	1.1312	0.0041	124.4	4.1
Coca leaf	2 June 1993	Bolivia	CAMS	−29.4	1.1326	0.0045	125.7	4.5
Coca leaf	5 September 1993	Colombia	CAMS	−28.9	1.1112	0.0044	104.5	4.4
Coca leaf	18 October 1993	Colombia	CAMS	−28.9	1.109	0.0054	102.7	5.4
Coca leaf	1 June 1994	Peru	CAMS	−28.9	1.1254	0.0050	118.9	5.0
Coca leaf	1 June 1994	Peru	CAMS	−30.9	1.1032	0.0046	96.7	4.6
Coca leaf	1 June 1994	Peru	CAMS	−30.0	1.1298	0.0045	123.3	4.5
Coca leaf	1 June 1994	Peru	CAMS	−28.7	1.1313	0.0043	124.8	4.3
Coca leaf	1 January 2000	Colombia	CAMS	−29.2	1.0777	0.0043	71.2	4.3
Coca leaf	1 January 2000	Colombia	CAMS	−30.2	1.0927	0.0052	86.1	5.2
Coca leaf	4 October 1993	Colombia	Keck	−29.6	1.1274	0.0025	119.4	2.5
Coca leaf	13 February 2003	Colombia	Keck	−29.1	1.0893	0.0022	81.5	2.2
Coca leaf	9 May 2003	Colombia	Keck	−29.6	1.0868	0.0022	79.0	2.2
Coca leaf	9 December 2003	Colombia	Keck	−29.4	1.0806	0.0024	72.9	2.4
Coca leaf	25 November 2004	Colombia	Keck	−38.2	1.0811	0.0022	73.4	2.2
Coca leaf	1 November 2006	Colombia	Keck	−29.1	1.0706	0.0025	63.0	2.5
Coca leaf	1 January 2007	Colombia	Keck	−29.4	1.0712	0.0033	62.1	3.3
Coca leaf	1 March 2007	Colombia	Keck	−28.3	1.0620	0.0033	47.1	4.0
Coca leaf	1 April 2007	Colombia	Keck	−29.9	1.0677	0.0030	58.1	3.2
Coca leaf	1 June 2007	Colombia	Keck	−29.7	1.0691	0.0030	60.5	3.1
Coca leaf	1 July 2007	Colombia	Keck	−29.7	1.0666	0.0023	56.9	3.3
Coca leaf	10 August 2007	Colombia	Keck	−27.4	1.0706	0.0030	55.6	3.1
Coca leaf	20 September 2007	Colombia	Keck	−27.9	1.0705	0.0032	50.3	3.2
Coca leaf	1 November 2007	Colombia	Keck	−27.0	1.0616	0.0033	56.6	3.3
Coca leaf	1 December 2007	Colombia	Keck	−27.7	1.0616	0.0030	53.4	3.1
Coca leaf	1 February 2008	Colombia	Keck	−27.8	1.0600	0.0022	52.4	2.2
Coca leaf	1 March 2008	Colombia	Keck	−27.6	1.0586	0.0022	51.0	2.2
Coca leaf	22 April 2008	Colombia	Keck	−28.1	1.0615	0.0021	54.0	2.1
Coca leaf	15 May 2008	Colombia	Keck	−28.8	1.0599	0.0021	52.4	2.1
Coca leaf	15 May 2008	Colombia	Keck	−28.1	1.0666	0.0031	54.7	3.2
Coca leaf	9 June 2008	Colombia	Keck	−28.1	1.0561	0.0022	48.6	2.2
Coca leaf	15 July 2008	Colombia	Keck	−28.3	1.0538	0.0022	46.3	2.2
Coca leaf	31 July 2008	Colombia	Keck	−29.9	1.0612	0.0023	53.6	2.3
Coca leaf	1 September 2008	Colombia	Keck	−29.0	1.0632	0.0022	55.6	2.2
Coca leaf	15 October 2008	Colombia	Keck	−29.3	1.0524	0.0024	44.9	2.4
Coca leaf	15 November 2008	Colombia	Keck	−28.9	1.0690	0.0027	61.4	2.7
Coca leaf	10 December 2008	Colombia	Keck	−29.3	1.0633	0.0023	55.7	2.3
Coca leaf	22 January 2009	Colombia	Keck	−27.9	1.0605	0.0023	52.9	2.3
Coca leaf	16 February 2009	Colombia	Keck	−28.7	1.0604	0.0023	52.9	2.3
Coca leaf	16 February 2009	Colombia	Keck	−29.2	1.0636	0.0023	56.1	2.3
Coca leaf	17 February 2009	Colombia	Keck	−29.1	1.0572	0.0022	49.7	2.2
Coca leaf	17 February 2009	Colombia	Keck	−29.3	1.0601	0.0023	52.6	2.3
Coca leaf	17 February 2009	Colombia	Keck	−29.4	1.0566	0.0026	49.1	2.6
Coca leaf	18 February 2009	Colombia	Keck	−28.6	1.0613	0.0026	53.7	2.6
Coca leaf	18 February 2009	Colombia	Keck	−28.6	1.0607	0.0023	53.2	2.3
Coca leaf	18 February 2009	Colombia	Keck	−29.7	1.0656	0.0026	58.0	2.6
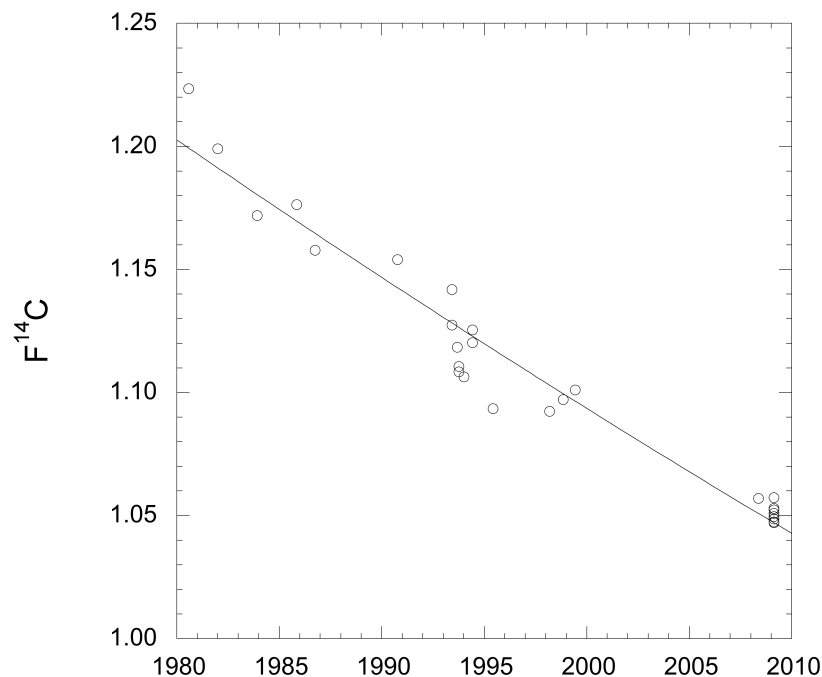
Figure 1 The $F^{14}C$ values of cocaine seized at field locations in Bolivia, Colombia, Ecuador, and Peru over a 3-decade time period. When multiple samples were acquired for the same decimal date, the mean $F^{14}C$ value was plotted. The exponential equation that best describes these data is $F^{14}C = 14776 \times e^{-0.0047557(year)}$, $R^2 = 95.8\%$.

We place our $\Delta^{14}C$ observations in the context of other $\Delta^{14}C$ previously published observations in Figure 2. We plot the $\Delta^{14}C$ observations from this study (coca leaf and cocaine base) versus previous time series observations for Schauinsland, average observations for the Southern Hemisphere, and average global observations as summarized by Hua and Barbetti (2004). From these combined data,

$$\Delta^{14}C_{all} = k \times e^{mT} \tag{8}$$

where $k = 1.5115 \times 10^{47}$, $m = -0.052$, and $r^2 = 0.967$. It is clear that the 6 oldest cocaine base specimens fell below the observed atmospheric $\Delta^{14}C$ values in the 1980–1990 time period. We have no explanation for why these specific $\Delta^{14}C$ values were lower than expected based on atmospheric observations from both hemispheres and the global averages (Figure 2). These 6 lower-than-expected observations represent samples from 4 different countries (Bolivia, Colombia, Ecuador, and Peru), but without a clear country-of-origin related pattern. However, from 1990–2000, the $\Delta^{14}C$ observations in this study were consistent with atmospheric data sets. Our observations from 2000–2009 extend previous observations along a trajectory predictable from previous atmospheric observations.

While these $\Delta^{14}C$ calibration curves allowed determination of the statistical-average age of coca leaf and cocaine base specimens produced for the time period 1980–2009, the time resolution is becoming weaker over time as bomb-derived atmospheric $^{14}CO_2$ is absorbed within the global carbon cycle. Nevertheless, the coca leaf $\Delta^{14}C$ calibration curve can be used to predict the ages of botanical tissues collected in northern portions of South America today and possibly extended to other tropical locations in the region for the next 5–10 yr. In fact, the utility of $F^{14}C$ and $\Delta^{14}C$ measurements
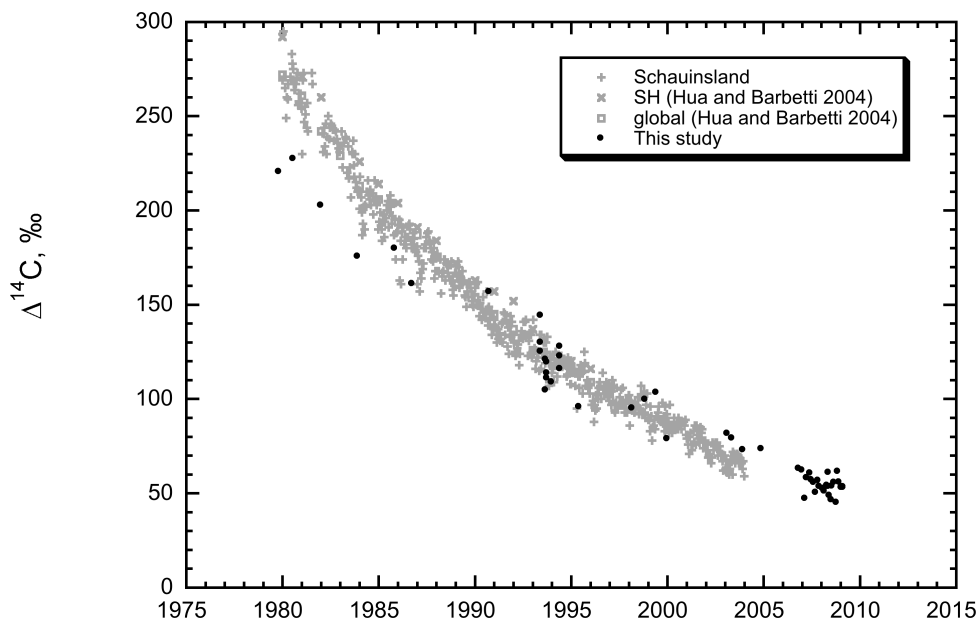
Figure 2 The $\Delta^{14}C$ values of coca leaves from field locations in Colombia, Bolivia, and Peru (1993–2009) and of cocaine base (1979–2009, measured value +8.8‰) from Colombia, Bolivia, Peru, and Ecuador compared to other global $\Delta^{14}C$ data sets representing Schauinsland, the Southern Hemisphere, and global averages as summarized by Hua and Barbetti (2004).

for aging modern samples could be longer given that the increasing contribution of fossil-fuel CO_2 into today's atmosphere.

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