1 Capabilities of the Lamont-Doherty Earth Observatory *in situ* [14]C extraction
2 laboratory updated
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9 Abstract

10   We report on the status and capabilities of the Lamont-Doherty Earth Observatory

11 *in situ* [14]C extraction laboratory. In late 2006 we began, in collaboration with the AMS

12 group at the University of Arizona, construction of a new laboratory to extract *in situ*

13 cosmogenic ^{14}C from terrestrial silicates. Long-term measurements of the process blank

14 over the last two years give an arithmetic mean and standard deviation of $125\pm43\times10^3$

15 atoms [14]C (*n*=9) and show significant improvement in the number of atoms, as well as

16 stability compared to initial measurements of the process blank. We report long-term

17 measurements of the intercomparison material CRONUS-A, which has been developed

18 as part of the CRONUS-Earth effort to characterize inter- and intra-laboratory variability.

19 We interpret the standard deviation (5%) of six replicate measurements of CRONUS-A

20 as the reproducibility of *in situ* [14]C extractions in our laboratory.

21 Introduction

22   Like the other commonly measured cosmogenic nuclides, ^{14}C is produced *in situ* in

23 earth surface materials by secondary cosmic rays. *In situ* [14]C has a number of advantages

24 over the other commonly measured cosmogenic nuclides: It has the shortest half-life

25 (5730 yrs), making it uniquely suited to address a number of questions either on its own

26 or in concert with a longer-lived nuclide (e.g., paired [10]Be-^{14}C measurements).

27 Production of *in situ* [14]C in quartz is at a rate approximately three times that of [10]Be

28   (Dugan et al., 2008; Lifton et al., 2001; Miller et al., 2006; Schimmelpfennig et al., 2012).

29   The measurement sensitivity of ^{14}C is currently greater than all of the other cosmogenic

30   nuclides, except for ^{3}He, and the abundance of accelerator mass spectrometry (AMS)

31   facilities with ^{14}C measurement capability is far greater than for the other nuclides. The

32   above factors make in situ^{14}C a potentially powerful tool in the study of earth surface

33   processes.

34   The most promising application of *in situ* ^{14}C is when it is paired with one or

35   more longer-lived cosmogenic nuclides to investigate complex exposure histories during

36   the past ca. 30 ka. To date only a few studies using *in situ* ^{14}C have been published, all

37   but one in the field of glacial geology (Anderson et al., 2008; Goehring et al., 2011;

38   Miller et al., 2006; White et al., 2011), the other used *in situ* ^{14}C to assess inherited ^{10}Be

39   (Matmon et al., 2005). Further potential applications of this paired nuclide approach are

40   broad and include studies of soil column overturning rates/depths (Fülöp et al., 2009;

41   Hippe et al., 2012; Lal et al., 1996), and paleoseismology (Handwerger et al., 1999). The

42   refinement of models of nucleon scaling is another promising field for *in situ* ^{14}C due to

43   its relatively rapid achievement of secular equilibrium (Brook et al., 1995; Lifton et al.,

44   2008). Determinations of the ^{14}C production rates in quartz are also scarce (Dugan et al.,

45   2008; Lifton et al., 2001; Miller et al., 2006; Schimmelpfennig et al., 2012). The paucity

46   of studies employing *in situ* ^{14}C reflects both the limited number of laboratories with *in*

47   *situ* ^{14}C extraction capabilities and the challenge of low-background extraction (Fülöp et

48   al., 2010; Goehring et al., 2008; Hippe et al., 2009; Lifton et al., 2001; Pigati et al., 2010).

49   In 2006 we began construction of a new *in situ* ^{14}C laboratory at Lamont-Doherty

50   Earth Observatory of Columbia University (LDEO). Development of the laboratory

51   facilities is complete and in a stable operating mode since 2010. Here we report on

52   progress made in the laboratory, including blank levels, improvements in precision, and

53   measurements of a recently developed intercomparison material.

54   Lab Design and Extraction Procedures

55   All extraction, purification, and graphitization lines are based on the designs of

56   Lifton et al. (2001) and Pigati et al. (2010). The laboratory is comprised of three main

57   systems, a flow-through extraction line (Pigati et al., 2010), a purification line (Lifton,

58   2001), and dedicated *in situ* [14]C graphitization line (Slota et al., 1987).

59   Extraction of *in situ* [14]C from quartz and preparation for AMS analysis is a three-

60   day process and follows the procedure outlined in Pigati et al. (2010). Day one consists of

61   a 1 hour 1200°C combustion of the lithium meta-borate ($LiBO_2$) flux and alumina

62   combustion boat to remove any surface contaminants and initially degass the $LiBO_2$. The

63    $LiBO_2$ is used to reduce the quartz fusion temperature during the subsequent sample

64   combustion (Lifton et al., 2001). Day one $LiBO_2$ combustion is done at 1200°C to ensure

65   release of all potential contaminants; however, combustion at 1100°C, which is the

66   sample combustion temperature should be equally effective. All evolved carbon species

67   are converted to CO_2 under a 5 sccm flow of ultra-high-purity O_2 held at 50 torr (~6.7

68   kPa) via interaction with 2-mm quartz beads within a u-tube furnace held at 1000°C. This

69   removes surface and atmospheric carbon contaminates from the flux as well as the

70   combustion boat and quartz sleeve, which protects the mullite furnace tube from the

71   volatile $LiBO_2$. On day two, ~5 g of quartz is added to the combustion boat and the

72   sample and flux are heated at 500°C for 1 hour to remove atmospheric carbon

73   contaminates, again in the presence of a 5 sccm flow of O_2. The sample is then heated at

74   1100°C for two hours in the presence of 50 torr (~6.7 kPa; static) of O_2, this melts the

75    $LiBO_2$ and dissolves the quartz, releasing carbon. Following the initial two hour

76   combustion, the sample is held at 1100°C for another hour in the presence of a 5 sccm

77   flow of O_2, while a 50 torr (~6.7 kPa) tube pressure is maintained. All evolved CO_2 is

78   collected in a liquid nitrogen-cooled coil trap and transferred to a flame-cleaned breakseal

79   for subsequent gas purification. Day three involves the purification of the CO_2 by

80   cryogenic removal of contaminant species (e.g. H_2O, NO_x, SO_2, SO_x, and halides). The

81   total evolved CO_2 is measured using a capacitance manometer (MKS Type 622A, 0-100

82   torr, ±0.25% full-range precision), diluted with ^{14}C-dead CO_2 to facilitate graphitization

83   for AMS analysis (typical samples are only 20-50 μg of C, blanks 5-10 μg C), and split

84   into two breakseals for AMS and $\delta^{13}C$ measurement. The AMS split is then converted to

85   graphite using catalytic reduction following Slota (1987). For data presented here, the

86   [14]C/13C ratio is measured by both AMS facilities.

87   Blank Measurements

88   All measurements (atoms and atoms g^{-1}) reported below were converted from

89   fraction modern values following the procedure outlined in Hippe et al. (in press). The

90    $\delta^{13}C$ correction included in the AMS laboratory reported fraction modern values is

91   removed, as is reporting of the fraction modern value relative to 1950 AD. This yields

92   carbon isotopic ratios relative to the isotopic ratio of the standard used in the AMS

93   measurement (Ox-II here). Reported averages and uncertainties are arithmetic means and

94   standard deviations. Sample concentrations are corrected for the long-term average blank.

95   Contamination from atmospheric, organic, and inorganic ^{14}C sources is

96   potentially a large source of the measured ^{14}C in a sample. The measurement of

97 numerous process blanks with stable and low background levels is therefore critical to

98 maximizing precision, confidence in the blank correction, and lowering the detection

99 limit. The practice of bracketing samples, approximately every five, with measurements

100 of the process blank are needed, because process blank measurements cannot be done

101 simultaneously with sample extraction. Figure 1 shows the evolution of blank

102 measurements at LDEO through time. The observed trend displays an overall reduction

103 in background ^{14}C by ~60%. It is difficult to attribute the reduction in background to a

104 given cause except for more thorough cleaning of the sacrificial quartz sleeve prior to

105 insertion into the furnace, along with diligent cleaning and handling of other quartz

106 implements entering the furnace. This conclusion is supported by the observation that

107 blank levels show a positive correlation with the total mass of carbon evolved during the

108 extraction procedure (Figure 2). It may however simply be due to progressive removal of

109 contaminant carbon in the line itself through repeated use, as has been suggested for other

110 similar *in situ* ^{14}C systems (Fülöp et al., 2010; Hippe et al., 2009). Regardless of the exact

111 cause of improvement in process blank levels, process blanks since January 2010 range

112 between $54\pm13\text{x}10^3$ and $179\pm51\text{x}10^3$ atoms ^{14}C with an average and standard deviation of

113 $125\pm42\text{x}10^3$ atoms ^{14}C (*n*=9) for these blanks. Blanks from January 2010 and later are

114 used as this represents the beginning of consistent use of the line and therefore likely

115 represent the true characteristic value for the process blank. Our process blank level is

116 commensurate with blank levels reported for similar line designs (Fülöp et al., 2010;

117 Lifton et al., 2001; Miller et al., 2006; Pigati, 2004).

118 Capabilities

119   Figure 3 shows the relationship between total uncertainty and ^{14}C concentration

120   measured at LDEO covering a range between 10×10^3 and 680×10^3 atoms g^{-1}. The overall

121   relationship is roughly an inverse exponential. At concentrations greater than

122   approximately 100×10^3 atoms g^{-1} there is no strong correlation. The observed relationship

123   is a result of both AMS measurement uncertainty and the large influence of the blank

124   correction on low concentration samples. At concentrations $>200 \times 10^3$ atoms g^{-1}, the

125   resulting analytical uncertainty is dominated by AMS counting statistics; however, as

126   concentrations fall below the "threshold" of $\sim 100 \times 10^3$ atoms g^{-1}, analytical uncertainties

127   increase exponentially as a result of a large blank correction, in addition to any larger

128   AMS uncertainties. From this, the effective detection limits of *in situ* ^{14}C measurements

129   for our line can be established. Two samples in particular show that concentrations below

130      $\sim 30 \times 10^3$ atoms g^{-1} yield very large uncertainties and in some cases are not statistically

131   different from 0.

132   CRONUS-A Measurements

133   To assess intra-laboratory measurement variability, we measured one of the

134   CRONUS-Earth intercomparison materials, CRONUS-A. Results of six measurements of

135   CRONUS-A by two operators over an approximately two-year period are presented in

136   Table 2 and Figure 4. All measurements are indistinguishable within 1-sigma

137   uncertainties with the exception of one low measurement. The resulting mean

138   concentration including all measurements is $652 \pm 33 \times 10^3$ atoms g^{-1}. We interpret the

139   standard deviation of $\sim 5\%$ to represent the intra-laboratory reproducibility of *in situ* ^{14}C

140   extractions from samples with a similar concentration to CRONUS-A. It is possible that a

141   lower concentration will yield more scatter; however, a lower concentration

142 intercomparison material (CRONUS-N) yields effectively zero ^{14}C atoms g^{-1} for the *in*

143 *situ* ^{14}C concentration and therefore the relationship between scatter and concentration is

144 unable to be established. A more recently developed intercomparison material,

145 CRONUS-R, should yield a lower measured concentration than CRONUS-A, and

146 hopefully greater than CRONUS-N, and may provide insight into any correlation

147 between concentration and scatter.

148 Conclusions

149   We have successfully constructed an *in situ* ^{14}C extraction laboratory at Lamont-

150 Doherty Earth Observatory based on the designs of Pigati (2004) and Lifton et al. (2001),

151 significantly increasing the potential number of *in situ* ^{14}C measurements made. During

152 the last two years, blank levels have been low, commensurate with similar laboratories,

153 and show good stability. Potential analytical uncertainty is very good and shows little

154 dependence on concentration above a threshold value of about 100 x 10^3 atoms g^{-1}. Intra-

155 laboratory scatter, as determined from repeat measurements of an inter-laboratory

156 comparison material is ~5%. Development of the Lamont-Doherty Earth Observatory

157 represents a significant advancement in the potential use of *in situ* ^{14}C in studies of earth

158 surface processes and landform dating, with many applications only presently being

159 realized.

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165   LDEO Publication xxxx.

166   References

167   Anderson, R.K., Miller, G.H., Briner, J.P., Lifton, N.A., DeVogel, S.B., 2008. A
168   millennial perspective of Arctic warming from ^{14}C in quartz and plants emerging from
169   beneath ice caps. Geophys. Res. Lett. 35, doi: 10.1029/2007GL03057.
170   Brook, E.J., Brown, E.T., Kurz, M.D., Ackert, J., Robert P., Raisbeck, G., Yiou, F., 1995.
171   Constraints on age, erosion, and uplift of Neogene glacial deposits in the Transantarctic
172   Mountains determined from in situ cosmogenic ^{10}Be and ^{26}Al. Geology 23, 1063-1066.
173   Dugan, B., Lifton, N., Jull, A.J.T., 2008. New production rate estimates for in situ
174   cosmogenic C-14. Geochim. Cosmochim. Acta 72, A231-A231.
175   Fülöp, R.-H., Bishop, P., Fabel, D., Cook, G.T., Schnabel, C., Naysmith, P., Xu, S., 2009.
176   Determining amounts and timing of soil erosion using in situ cosmogenic ^{14}C and ^{10}Be.
177   Geochimica Et Cosmochimica Acta Supplement 73, A403.
178   Fülöp, R.H., Naysmith, P., Cook, G.T., Fabel, D., Xu, S., Bishop, P., 2010. Update on the
179   Performance of the Suerc in Situ Cosmogenic C-14 Extraction Line. Radiocarbon 52,
180   1288-1294.
181   Goehring, B.M., Schaefer, J.M., Lifton, N., Jull, A.J.T., 2008. Progress and Initial Results
182   from the Lamont-Doherty Earth Observatory in situ Carbon-14 Extraction Laboratory,
183   Accelerator Mass Spectrometry 11 Meeting, Rome, Italy.
184   Goehring, B.M., Schaefer, J.M., Schluechter, C., Lifton, N.A., Finkel, R.C., Jull, A.J.T.,
185   Akçar, N., Alley, R.B., 2011. The Rhone Glacier was smaller than today for most of the
186   Holocene. Geology 39, 679-682.
187   Handwerger, D.A., Cerling, T.E., Bruhn, R.L., 1999. Cosmogenic 14C in carbonate rocks.
188   Geomorph. 27, 13-24.
189   Hippe, K., Kober, F., Baur, H., Ruff, M., Wacker, L., Wieler, R., 2009. The current
190   performance of the in situ ^{14}C extraction line at ETH. Quat. Geochron. 4, 493-500.
191   Hippe, K., Kober, F., Wacker, L., Fahrni, S.M., Ivy-Ochs, S., Akcar, N., Schluchter, C.,
192   Wieler, R., in press. An update on in situ cosmogenic ^{14}C analysis at ETH Zürich. Nucl.
193   Instrum. Methods.
194   Hippe, K., Kober, F., Zeilinger, G., Ivy-Ochs, S., Maden, C., Wacker, L., Kubik, P.W.,
195   Wieler, R., 2012. Quantifying denudation rates and sediment storage on the eastern
196   Altiplano, Bolivia, using cosmogenic ^{10}Be, ^{26}Al, and in situ ^{14}C. Geomorph.
197   Lal, D., Pavich, M., Gu, Z.Y., Jull, A., 1996. Recent Erosional History of a Soil Profile
198   Based on Cosmogenic In-Situ Radionuclides ^{14}C and ^{10}Be. Geophysical Monograph 95,
199   371-376.
200   Lifton, N., Smart, D., Shea, M., 2008. Scaling time-integrated in situ cosmogenic nuclide
201   production rates using a continuous geomagnetic model. Earth Planet. Sci. Lett. 268, 190-
202   201.
203   Lifton, N.A., Jull, A.J.T., Quade, J., 2001. A new extraction technique and production
204   rate estimate for in situ cosmogenic ^{14}C in quartz. Geochim. Cosmochim. Acta 65, 1953-
205   1969.

206 Matmon, A., Shaked, Y., Porat, N., Enzel, Y., Finkel, R., Lifton, N., Boaretto, E., Agnon,
207 A., 2005. Landscape development in an hyperarid sandstone environment along the
208 margins of the Dead Sea fault: Implications from dated rock falls. Earth Planet. Sci. Lett.
209 240, 803-817.
210 Miller, G.H., Briner, J.P., Lifton, N.A., Finkel, R.C., 2006. Limited ice-sheet erosion and
211 complex exposure histories derived from in situ cosmogenic [10]Be, [26]Al, and ^{14}C on Baffin
212 Island, Arctic Canada. Quat. Geochron. 1, 74-85.
213 Pigati, J.S., 2004. Experimental Developments and Application of Carbon-14 and in situ
214 Cosmogenic Nuclide Dating Techniques, Department of Geosciences. University of
215 Arizona, Tucson, AZ, p. 188.
216 Pigati, J.S., Lifton, N.A., Jull, A.J.T., Quade, J., 2010. A Simplified In Situ Cosmogenic
217 [14]C Extraction System. Radiocarbon 52, 1236-1243.
218 Schimmelpfennig, I., Schaefer, J., Goehring, B.M., Lifton, N., Putnam, A., 2012.
219 Calibration of the in-situ ^{14}C production rate in the Southern Alps, New Zealand. J. Quat.
220 Sci. 27, 671-674.
221 Slota, P.J., Jr., Jull, A.J.T., Linick, T.W., Toolin, L.J., 1987. Preparation of small samples
222 for ^{14}C accelerator targets by catalytic reduction of CO. Radiocarbon 29, 303-306.
223 White, D., Fülöp, R.-H., Bishop, P., Mackintosh, A., Cook, G., 2011. Can in-situ
224 cosmogenic 14C be used to assess the influence of clast recycling on exposure dating of
225 ice retreat in Antarctica? Quat. Geochron. 6, 289-294.
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Tables

Table 1. Process blank measurement information. Columns are the volume of CO_2 extracted from the sample, mass of carbon extracted, volume of the diluted sample, measured fraction modern, and number of ^{14}C atoms. Fm values measured relative to Ox-II. All blank measurements assume a $\delta^{13}C$ value of -17.6±0.17 ‰ unless otherwise noted, which is based on numerous measurements of our dilution CO_2 and effectively dominates the measured $\delta^{13}C$ value due to the large dilution factor. ^{14}C measurements were either made at the University of Arizona (UA) or the Lawrence-Livermore Center for Accelerator Mass Spectrometry (CAMS).

Date	AMS Lab	V_{CO2} (10^{-2} cc STP)	Mass C (μg)	$V_{diluted}$ (10^{-2} cc STP)	Fm_{Meas}	$\delta^{13}C$ (‰)	^{14}C (10^3 atoms)
7/7/08	UA	2.36±0.02	12.65±0.08	131.91±0.88	0.0236±0.0006	-	903.79±54.31
7/9/08	UA	2.67±0.02	14.28±0.10	131.26±0.88	0.0138±0.0005	-	494.67±52.40
					Average	-	699.23±289.29
1/26/09	UA	1.50±0.02	8.01±0.09	127.62±1.46	0.0075±0.0012	-	212.80±67.74
2/19/09	UA	1.91±0.02	10.21±0.12	158.87±1.82	0.0097±0.0012	-	391.38±83.90
					Average	-	302.09±126.27
1/30/10	UA	1.73±0.01	9.24±0.08	251.56±2.13	0.0035±0.0002	-17.474±0.004	169.05±93.36
2/11/10	UA	1.52±0.02	8.16±0.09	147.07±1.68	0.0051±0.0003	-17.569±0.007	144.48±56.28
3/5/10	UA	1.24±0.01	6.63±0.08	114.41±1.32	0.0057±0.0002	-	132.90±43.07
3/29/10	UA	1.78±0.02	9.54±0.11	137.18±1.57	0.0059±0.0002	-	178.68±51.29
7/28/10	CAMS	1.29±0.02	6.89±0.08	142.17±1.64	0.0045±0.0001	-	89.28±13.02
1/11/11	CAMS	1.27±0.01	6.80±0.08	140.45±1.61	0.0037±0.0001	-	53.65±12.76
1/13/11	CAMS	1.30±0.02	6.94±0.08	138.01±1.59	0.0043±0.0001	-	79.44±12.71
5/11/11	CAMS	1.57±0.02	8.41±0.10	134.64±1.54	0.0061±0.0001	-	152.88±12.88
6/1/11	CAMS	1.67±0.02	8.93±0.10	137.81±1.58	0.0053±0.0001	-	121.66±13.12
					Average	-	124.67±42.56

Table 2. Measurements of the CRONUS-A intercomparison material. Columns are as in Table 1, except showing concentrations (atoms g^{-1}), rather than total atoms. $\delta^{13}C$ values for each sample are indicated, otherwise they are assumed to be -17.74±0.17 ‰, which is derived from the average of $\delta^{13}C$ values measured in quartz samples, but effectively is dominated by our dilution CO_2.

Sample ID	AMS Lab	Qtz Mass (g)	VCO_2 (10^{-2} cc STP)	Mass C (µg)	$V_{diluted}$ (10^{-2} cc STP)	Fm_{Meas}	$\delta^{13}C$ (‰)	^{14}C (10^3 at g^{-1})
CRONUS-A[1]	UA	5.0045	6.15±0.07	32.96±0.38	172.36±1.97	0.067±0.0013	-17.61±0.02	642.68±32.80
CRONUS-A-2[1]	UA	4.6503	6.00±0.07	32.11±0.37	125.00±1.43	0.075±0.0010	-17.49±0.01	591.54±17.88
CRONUS-A-NM-1	CAMS	4.9739	6.14±0.07	32.89±0.38	138.11±1.58	0.081±0.0005	-	657.51±12.58
CRONUS-A-NM-2	CAMS	4.9912	6.71±0.08	35.94±0.41	143.73±1.66	0.080±0.0004	-	679.54±12.69
CRONUS-A-3-19-11	CAMS	5.0050	7.59±0.09	40.66±0.47	143.30±1.64	0.081±0.0004	-	677.98±12.44
CRONUS-A-3-28-11	CAMS	5.0211	7.52±0.09	40.27±0.46	142.73±1.63	0.080±0.0004	-	664.33±12.29
							Average	652.26±32.7

[1] Blank correction based on blanks completed in 2009. All other CRONUS-A measurements are corrected for the mean blank 2010 and later.

Figure Captions

Figure 1. Plot of blank measurements versus time. Trend shows gradual improvement in blank levels and overall improvement in consistency. In all figures, errors are shown at one-sigma.

Figure 2. Blank levels versus total carbon evolved during a process blank. A correlation is observed between carbon mass and number of ^{14}C atoms.

Figure 3. Analytical uncertainty versus sample concentration.

Figure 4. Plot of all measurements of the CRONUS-A intercomparison material. Solid line indicates arithmetic mean of all values, shading is one standard deviation, dashed line indicates two standard deviations.
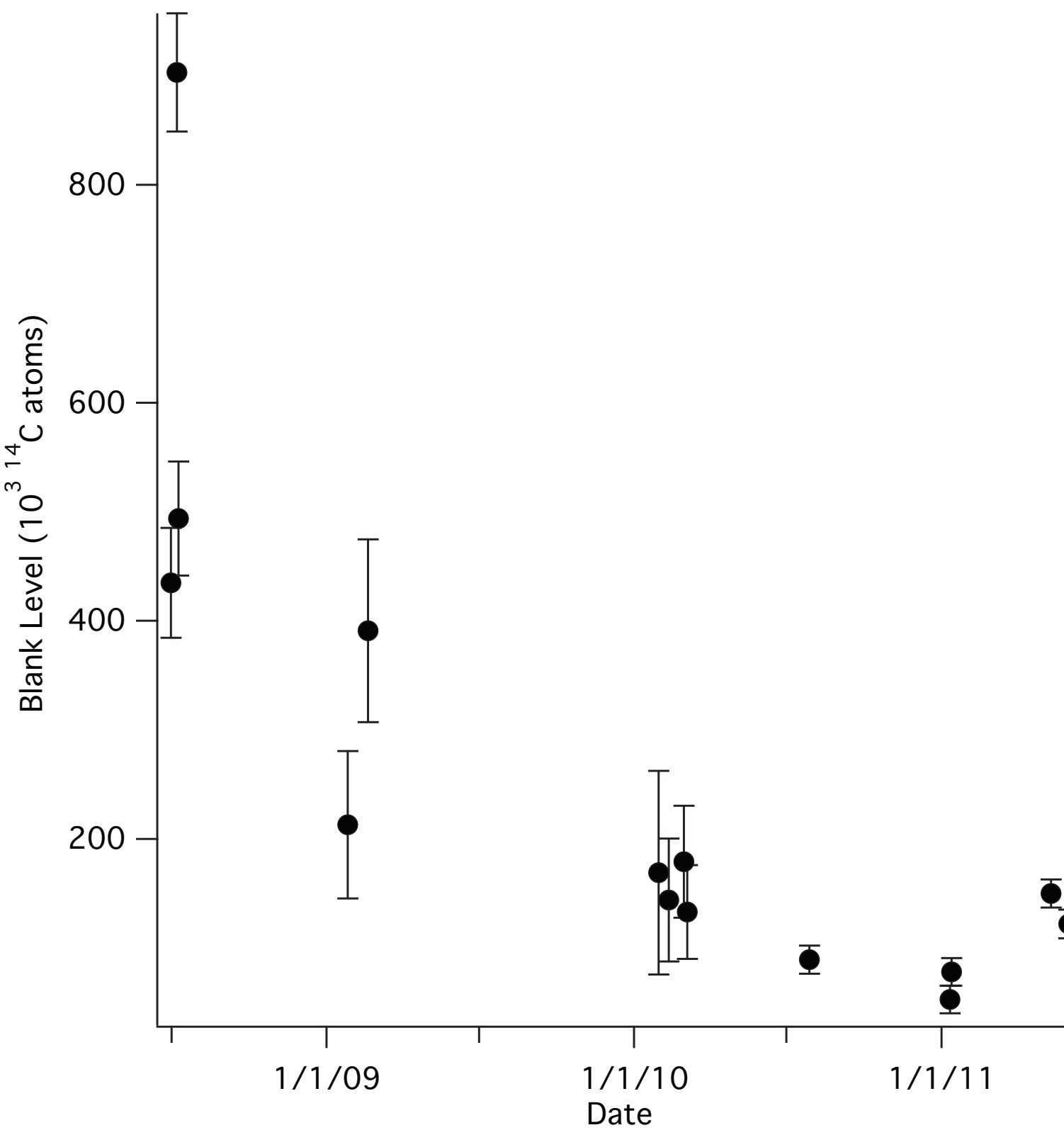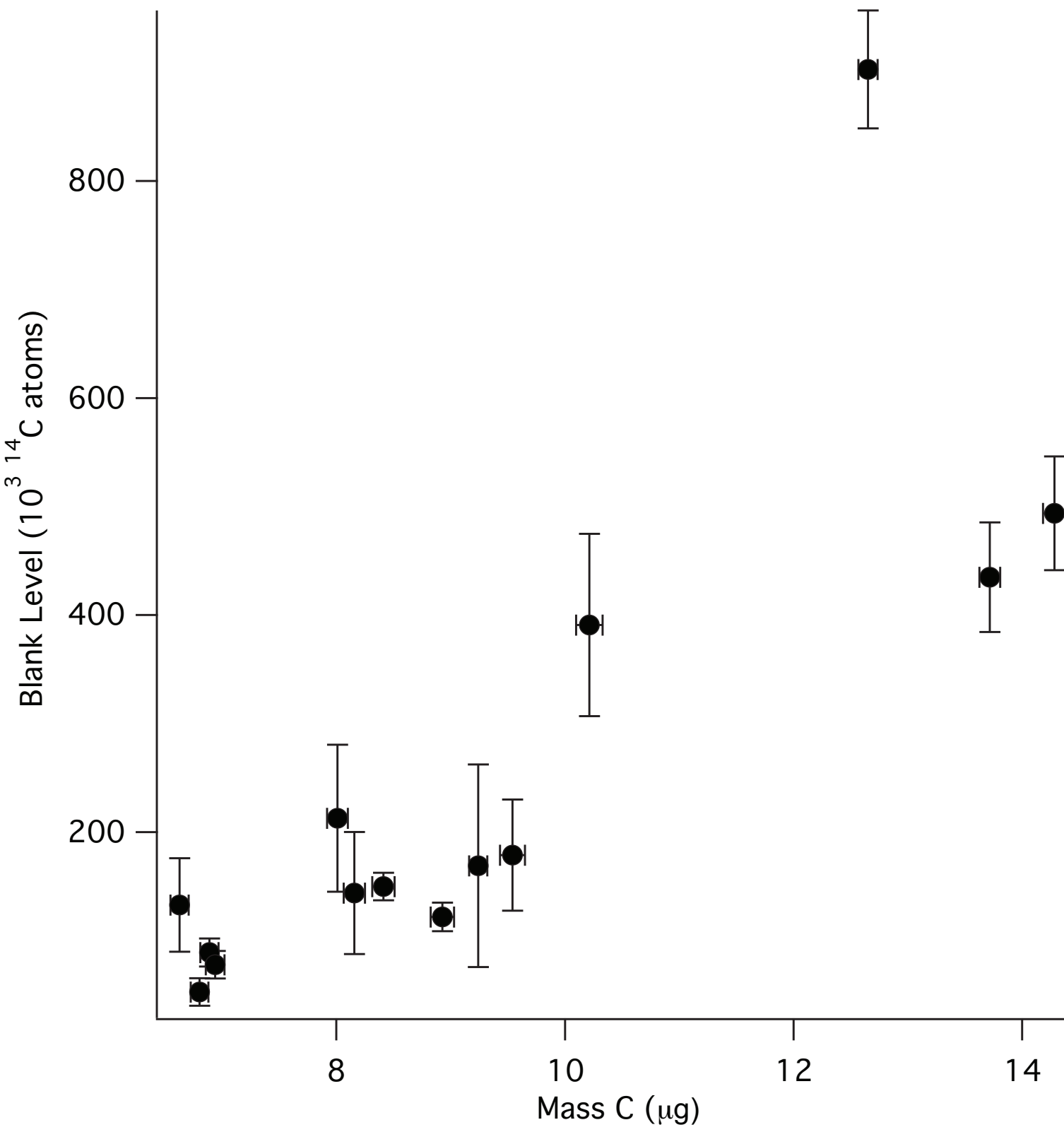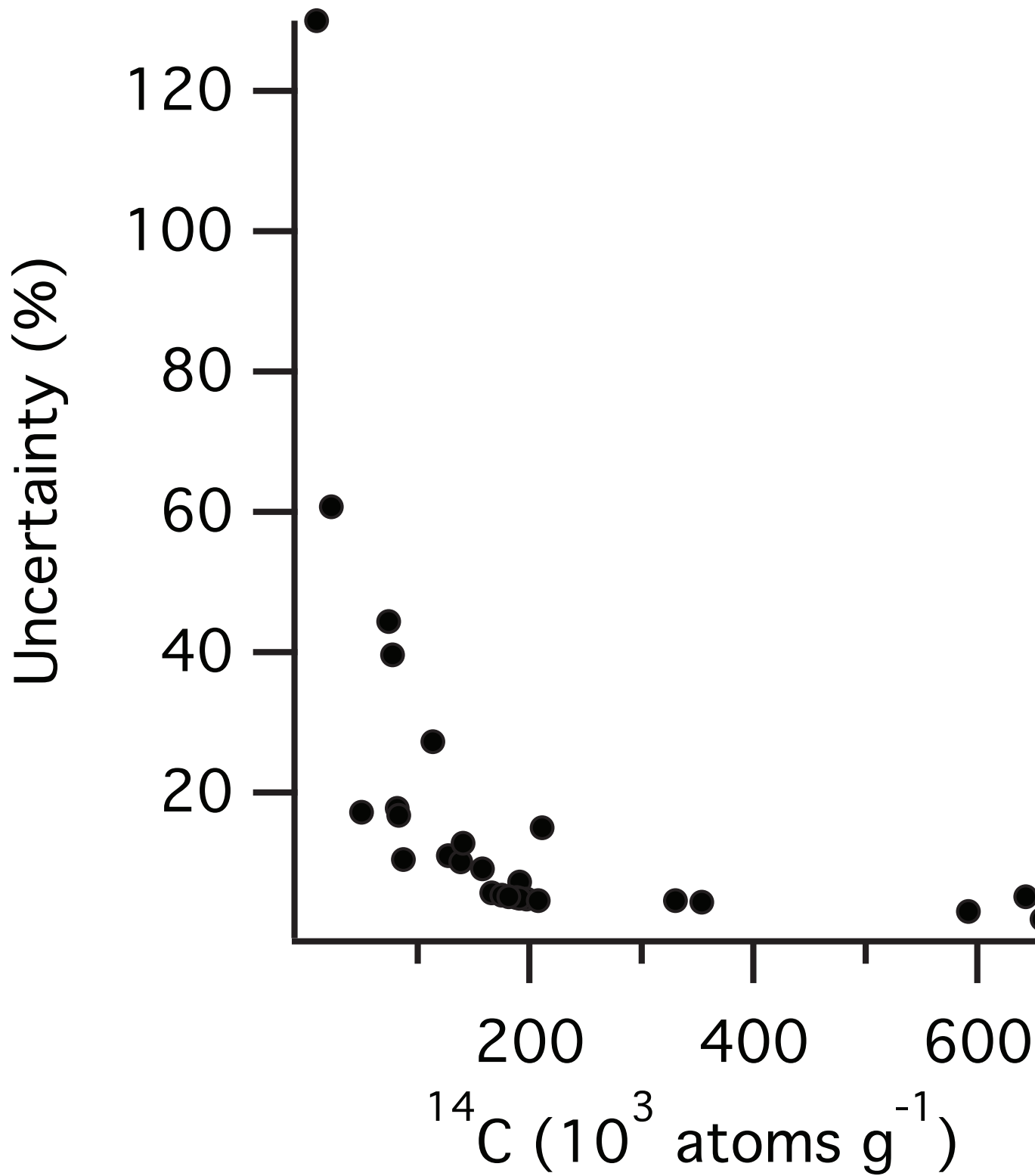
Figure 1

Figure 2

Figure 3

Figure 4