

1 **A highly portable and inexpensive field sampling kit for radiocarbon analysis of carbon dioxide**

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3

4 **ABSTRACT.** Radiocarbon (^{14}C) analysis of carbon dioxide (CO_2) can be extremely useful in carbon cycle
5 studies because it provides unique information that can infer the age and source of this greenhouse
6 gas. Cartridges containing the CO_2 -adsorbing zeolite molecular sieve are small and highly portable,
7 which makes them more suitable for field campaigns in remote locations compared to some other
8 CO_2 collection methods. However, sampling with molecular sieve cartridges usually requires
9 additional equipment, such as an infrared gas analyser, which can reduce portability and pose
10 limitations due to power demands. In addition, ^{14}C analysis of CO_2 is increasingly being used in field
11 experiments which require high numbers of replicate CO_2 collections, placing extra pressure on an
12 expensive and cumbersome collection apparatus. We therefore designed and built a molecular sieve
13 CO_2 sampling kit that utilises a small, low power CO_2 sensor. We demonstrate the reliability of the
14 new kit for the collection of CO_2 samples for ^{14}C analysis in a series of laboratory and field tests. This
15 inexpensive sampling kit is small, light-weight, highly portable, and has low power demands, making
16 it particularly useful for field campaigns in remote and inaccessible locations.

17

18 **INTRODUCTION**

19 The radiocarbon (^{14}C) concentration of carbon dioxide (CO_2) provides valuable information that can
20 be used to infer the age and source of this greenhouse gas and has become particularly useful in
21 studies concerning the Earth's carbon cycle (Wotte et al. 2017b). For example, the contribution of
22 fossil carbon sources (e.g. derived from fossil fuel combustion) to atmospheric CO_2 can be quantified
23 using $^{14}\text{CO}_2$ analyses (e.g. Levin and Hesshaimer 2000; Major et al. 2018; Zhou et al. 2020).
24 Measurements of ^{14}C in soil CO_2 emissions have been used to detect the release of aged carbon
25 within the modern carbon cycle (Kwon et al. 2019) and to explore the role of priming in the
26 decomposition of organic matter (Hartley et al. 2012; Street et al. 2020). Radiocarbon analysis of CO_2
27 evaded from water surfaces has indicated rapid cycling of aquatic carbon in some environments (e.g.
28 Campeau et al. 2019; Dean et al. 2020), but slower turnover in others (e.g. Billett et al. 2007).

29 Sample gases containing CO_2 can be collected for ^{14}C analysis using a variety of techniques. Glass
30 flasks, metal canisters or gas sample bags, all provide relatively straightforward and portable
31 methods for the collection of samples. However, at the relatively low CO_2 concentrations (<0.1 %)
32 that are typically encountered in many field sampling situations (e.g. studies of soil respiration or
33 aquatic CO_2 evasion) the volume of the storage vessel must be sufficient (e.g. >1 L) to ensure that
34 the sample requirements for ^{14}C analysis are met (e.g. 1 ml CO_2 for accelerator mass spectrometry).
35 Therefore, these sampling methods, and others relying on absorption of CO_2 in hydroxide solution
36 (e.g. Molnár et al. 2010), are far from ideal for field campaigns in remote locations with poor
37 accessibility, where transport of bulky equipment is challenging.

38 Cartridges containing zeolite molecular sieves provide an alternative sample CO_2 storage medium
39 which can overcome the limitations associated with other storage methods. Molecular sieves such
40 as zeolite Type 13X are porous, have high CO_2 -adsorbing capacity (Breck 1974), and enable enough
41 gas for ^{14}C analysis to be collected on just a few grams of zeolite (Garnett et al. 2019). Sampling
42 usually involves little more than pumping sample air through the molecular sieves using an air pump,

43 although removal of water using a chemical trap (e.g. magnesium perchlorate) is recommended since
44 water is also adsorbed by the zeolite and reduces the CO₂ adsorption capacity of the sieve (Bol and
45 Harkness 1995). Once trapped on the molecular sieve and isolated from the atmosphere the sample
46 CO₂ is stable and can be stored for many months before processing (Wotte et al. 2017b; Garnett et
47 al. 2019). Several kits for the collection of samples for determining the ¹⁴C content of CO₂ (¹⁴CO₂) that
48 incorporate molecular sieve cartridges have been reported in the literature (e.g. Gaudinski et al.
49 2000; Hardie et al. 2005; Hämäläinen et al. 2010; Palonen 2015; Wotte et al. 2017a). To ensure that
50 enough CO₂ has been collected for ¹⁴C analysis, these kits often include an instrument to monitor
51 CO₂ concentrations and, in most cases, an infrared gas analyser (IRGA) is used (e.g. PPSystems EGM4;
52 Hardie et al. 2005; LI-COR Li-840A; Palonen 2015). While IRGAs can provide extremely accurate
53 measurements of CO₂ concentration, their power requirements and expense can pose limitations.
54 Moreover, if the role of the instrument in a ¹⁴CO₂ sampling kit is simply to ensure that enough sample
55 has been trapped in a molecular sieve cartridge, then such a sensitive instrument may not be
56 essential.

57 ¹⁴CO₂ measurements are increasingly utilised in ecological experiments which require multiple
58 replicate measurements to detect statistical differences between control and treatment (Gavazov et
59 al. 2018; Hartley et al. 2012; Street et al. 2020). In addition, researchers are actively encouraged to
60 work in increasingly remote locations in order to increase the representativeness of their work
61 (Metcalf et al. 2018). These factors place pressure on the current CO₂ collection technology in both
62 their capacity to collect larger numbers of samples and their practicality in remote field locations.

63 Drawing upon recent innovations in small, low cost and low power CO₂ sensors, and the open source
64 electronics movement, we sought to build a molecular sieve ¹⁴CO₂ sampling kit that would
65 particularly benefit field sampling campaigns in remote locations and increase the capacity for
66 replicate sampling. Here, we describe a new sampling system (“Mini kit”) for the collection of CO₂
67 for ¹⁴C analysis which we have designed to be highly portable and affordable. We also report the
68 results of laboratory and field experiments used to test the reliability of the kit.

69

70 **MATERIALS AND METHODS**

71 **Description of the sampling system**

72 The Mini kit (Figure 1) consists of two main components: (i) a network of tubing that connects to the
73 sampling vessel (e.g. respiration chamber or incubation jar) and includes cartridges for removing
74 water and atmospheric CO₂ in the chamber prior to sample CO₂ accumulation, and to trap sample
75 CO₂ on molecular sieve, and (ii) a unit housing a CO₂ sensor and air pump that circulates the air from
76 the sampling vessel through the traps and enables the operator to monitor the chamber CO₂
77 concentration.

78 As also used in an established sampling kit (Garnett et al. 2019), water and atmospheric CO₂ are
79 removed from the air stream using cartridges containing magnesium perchlorate (Elemental
80 Microanalysis, UK) and soda lime (Fisher Scientific, UK), respectively, held in place using quartz wool.
81 These cartridges were made from quartz glass tube (OD 18 mm x 22 cm) which was stoppered at
82 both ends using one-hole rubber bungs. A 5 cm length of OD 6 mm glass tube was inserted into the
83 rubber bungs and a 5 cm length of Iso-versinic tubing (Saint-Gobain, France) pushed onto the glass
84 tubing. The cartridges were completed by inserting couplings (CPC; Colder Products Company, USA)
85 into the Iso-versinic tubing. The couplings automatically seal when disconnected, and we used them
86 on all cartridges and throughout the sampling kit where connections were required.

87 The molecular sieve cartridges have previously been described (see Garnett et al. 2019; Hardie et al.
88 2005). Briefly, they were composed of glass tubing with a central compartment containing 3–4 g of
89 zeolite molecular sieve (Type 13X, 1.6 mm pellets, Sigma-Aldrich, UK) held in place using stainless
90 steel wool. At either end of the cartridge were attached 5 cm lengths of Iso-versinic tubing and CPC
91 couplings, enabling connection to the sampling kit.

92 The pump/sensor unit (Figure 1b) contained a small air pump (D220 BL, TCS micropumps Ltd, UK)
93 and a SprintIR[®]-W CO₂ sensor (0–5% with flow through adaptor; Gas Sensing Solutions, UK). We
94 chose the SprintIR[®]-W, which is a non-dispersive infrared sensor, due to its low power requirements
95 (35 mW; www.gassensing.co.uk), fast response time and because the flow through adaptor is
96 convenient for creating air-tight connections to a network of tubing. The pump/sensor unit is
97 controlled by an Arduino Nano microcontroller (Arduino, Italy; www.arduino.cc) which handles
98 communication with the SprintIR[®]-W sensor and displays the CO₂ concentration on an organic light-
99 emitting diode (oled) display. We calibrate the SprintIR[®]-W CO₂ sensor immediately before use by
100 manually setting the 0-ppm point by circulating air through the pump/sensor unit and the cartridge
101 of soda lime in a closed loop (alternatively, calibration can be performed using fresh air or using a
102 gas with a known CO₂ concentration; www.gassensing.co.uk). A PP9 9v battery is used to provide
103 power for all components of the pump/sensor unit, which results in a flow rate of ca. 400–450
104 ml/min for the D220 BL air pump. Full details of the pump/sensor unit, including parts, schematics,
105 Arduino code and sampling procedures are presented in the Supplementary section.

106 To protect the CO₂ sensor from damp air during operation the cartridge containing the desiccant was
107 connected to the inlet of the pump/sensor unit (Figure 1c). After exiting the pump/sensor unit the
108 air stream can either be directed through the soda lime cartridge to remove atmospheric CO₂ from
109 the system, or through an empty glass tube when measurement of CO₂ concentrations are required;
110 this empty tube was replaced by a molecular sieve cartridge when collecting a sample of CO₂ for ¹⁴C
111 analysis. Clips (WeLoc, Scandinavia Direct, UK) placed on the Iso-versinic tubing were used to direct
112 sample gas and two ca. 2 m lengths of OD 6 mm nylon pneumatic air hose connected the Mini kit to
113 sampling vessels.

114

115 **Reliability for measurement of CO₂ concentration**

116 We tested the performance of the CO₂ sensor in the Mini kit by comparison with an IRGA in both lab-
117 and field-tests. In the lab test, the gas ports of the Mini-kit and an EGM4 IRGA were coupled together
118 in series with the exhaust of the Mini kit being routed to the inlet of the EGM4. A manifold upstream
119 of the Mini kit enabled the gas being analysed to be quickly swapped between 5 different sources:
120 a. atmospheric air brought in from outside via a nylon hose, b. a 10 L foil gas bag (SKC Ltd, UK)
121 containing pure N₂ gas, c. a 10 L foil gas bag containing laboratory air (790 ppm, independently
122 measured using an EGM5 IRGA; PPSystems, USA), d. CO₂-free atmospheric air brought in from
123 outside via a nylon tube and passed through a cartridge containing soda lime, e. a 10 L foil gas bag
124 containing an elevated CO₂ concentration (2200 ppm; independently measured using an EGM5
125 IRGA). The Mini kit SprintIR[®]-W CO₂ sensor and EGM4 were both connected to a computer and their
126 CO₂ concentrations logged at 1 s intervals. The source gas was manually swapped every ca. 1 min
127 and both the Mini kit SprintIR[®]-W CO₂ sensor and EGM4 were zero-calibrated at the start.
128 Manufacturer's specifications state an accuracy of <1% for CO₂ concentration measurements by the
129 EGM4 and EGM5 IRGAs.

130 The field test, conducted in November 2018, involved coupling the gas ports of the Mini kit with an
131 EGM5 IRGA and simultaneously logging the CO₂ concentration of a soil respiration chamber installed
132 on a grass lawn. The soil respiration chamber was constructed from 11 cm diameter plastic drainpipe,
133 22 cm high and inserted ca. 5 cm into the ground. Couplings installed in the chamber allowed
134 connection of gas lines so that chamber air could be circulated in a closed loop through the Mini kit
135 and the EGM5; the internal pump of the EGM5 was switched off and the Mini kit's pump used to
136 drive the air circulation. The SprintIR®-W CO₂ sensor in the Mini kit was zero-calibrated at the start
137 of the test only; the EGM5 was also zero-calibrated at the start and subsequently performed
138 automatic zero-point calibrations every 30 minutes. Since the EGM5 calibration involves diverting
139 the sample air through a soda lime column this caused a reduction in chamber CO₂ concentration
140 every 30 minutes. Flow rate of the air stream through the system was logged using the flow sensor
141 of the EGM5.

142 We simulated the collection of a CO₂ sample for radiocarbon analysis during the field test. This
143 involved firstly passing chamber air through the soda lime cartridge in order to remove the
144 contaminating influence of atmospheric CO₂ (CO₂ scrubbing). Scrubbing was performed for 20 min,
145 after which CO₂ build-up occurred in the chamber by diverting the air flow through the empty glass
146 tube instead of soda lime. The Mini kit and EGM5 monitored the CO₂ build-up in the chamber for
147 over 200 minutes whereupon the empty glass tube was replaced with a molecular sieve cartridge
148 and chamber CO₂ was collected. Air temperature was ca. 5°C.

149

150 **Reliability for measurement of radiocarbon concentration of CO₂**

151 The reliability of the Mini-kit for collecting CO₂ samples for radiocarbon analysis was tested using
152 two approaches. First, the Mini kit was used to sample CO₂ standards of known ¹⁴C concentration.
153 The CO₂ standards were provided in OD 6 mm flame-sealed glass tubes after being generated from
154 the following reference materials: barley mash from the Third International Radiocarbon
155 Intercomparison (TIRI; 116.35 ± 0.0084 pMC; Gulliksen and Scott 1995), Belfast cellulose from the
156 Fourth International Radiocarbon Intercomparison (FIRI; 57.22 ± 0.04 pMC; Boaretto et al. 2002) and
157 Iceland spar calcite (laboratory internal ¹⁴C background standard). The glass tube containing the
158 standard was scored and placed inside a strong glass vessel (an empty standard wine bottle cleaned
159 using carbon-free detergent; Decon90®, Decon Laboratories Limited, UK) which acted as a chamber.
160 The bottle was sealed with a 2-hole rubber bung which contained two stainless steel gas sampling
161 ports with couplings that enabled connection to the Mini kit in a closed loop. Atmospheric CO₂ was
162 first scrubbed from the chamber by circulating the air via the soda lime cartridge. The CO₂ standard
163 was then released by smashing the glass tube against the wall of the wine bottle and then collected
164 onto a molecular sieve cartridge.

165 The second approach involved soil incubations and the collection of respired CO₂ using the Mini kit
166 and an established approach based around an EGM4 (Hardie et al. 2005; Garnett et al. 2019). Six
167 incubation vessels were produced using 1 L Schott bottles. Commercially available peat-based
168 compost (Verve sowing & cutting compost, B&Q, UK; 75.6 %moisture), was homogenised, and 100 g
169 placed into each incubation vessel. A glass fibre filter (GF/A, Whatman, UK) was placed over the
170 bottle opening to exclude atmospheric particulates. After storage in the dark at room temperature
171 for 2 d, the glass fibre filters were replaced with 2-hole rubber bungs that had stainless steel gas
172 sampling ports with couplings, making the vessels air-tight. The headspace of the vessels was
173 scrubbed using soda lime to remove atmospheric CO₂ and the vessels left overnight to allow CO₂ to
174 accumulate.

175 On the first sampling occasion we collected CO₂ from the headspace of 3 of the incubation vessels
176 with the Mini kit and the remaining 3 vessels with the EGM4-based kit. We then resealed vessels 2,
177 3 and 6 and sampled them for a second time 24 h later using the alternative sampling method so
178 that these three vessels were sampled using both sampling systems (e.g. vessel 2 was sampled with
179 the EGM4 system first and subsequently using the Mini kit on the second occasion).

180 Sample CO₂ was recovered from molecular sieve cartridges using routine methods at the NEIF
181 Radiocarbon Laboratory (Garnett et al. 2019). This involved purging the molecular sieve with high
182 purity N₂ (Research Grade 5.0, BOC, UK) for 15 minutes while heating at 425°C, followed by cryogenic
183 collection and purification of the evolved CO₂. The amount of CO₂ recovered was determined using
184 a pressure transducer on a calibrated volume and the sample split into aliquots for δ¹³C and ¹⁴C
185 measurement. Isotope ratio mass spectrometry was used to determine the δ¹³C of the sample CO₂
186 using a Delta V (Thermo-Fisher, Germany). The ¹⁴C aliquot was converted to graphite using Fe:Zn
187 reduction (Slota et al. 1987) and measured using accelerator mass spectrometry (AMS) at the
188 Scottish Universities Environmental Research Centre. Following convention (Stuiver and Polach
189 1977), all ¹⁴C results were corrected for isotopic fractionation by normalising to a δ¹³C of -25 ‰ using
190 the measured δ¹³C values and expressed as ‰modern carbon (pMC). Statistical tests were performed
191 using Minitab (version 19).

192

193 **RESULTS**

194 **Reliability for measurement of CO₂ concentration**

195 The laboratory test of CO₂ measurements by the Mini kit showed a high level of agreement with the
196 EGM4 and EGM5 IRGA values for the same gas (Figure 2). On average, the Mini kit reported a CO₂
197 concentration 39 ppm higher than the EGM4, which represented an average difference of 7% of the
198 gas concentration. The differences for individual reference gases A, C and E were 8%, 4% and 7%,
199 respectively. Although Figure 2 shows that the Mini kit CO₂ concentration measurements were
200 relatively noisy compared to the EGM4, the close tracking of the curves indicates that the
201 instruments responded very similarly to changes in the CO₂ concentration of the source gas.

202 In the field test, the Mini kit usually reported a slightly lower CO₂ concentration for the chamber air
203 compared to the EGM5, although the overall pattern of CO₂ concentration during the scrubbing, CO₂
204 build-up and collection phases was very similar (Figure 3). On average, the offset between the Mini
205 kit and EGM5 CO₂ measurements was 62 ppm, however, the agreement was closer (49 ppm) in the
206 first 200 minutes. During CO₂ collection the fall in chamber CO₂ concentration, which corresponds to
207 the volume of CO₂ collected in the molecular sieve trap, was very similar for both instruments (Mini
208 kit = 1150 ppm, EGM5 = 1132 ppm). Flow rate decreased from ca. 400 ml/min at the start of the
209 sampling to 380 ml/min after over 4 hours.

210

211 **Reliability for measurement of CO₂ radiocarbon concentration**

212 A total of 8 radiocarbon CO₂ standards were processed in the laboratory test of the Mini kit, ranging
213 in CO₂ volume from 2.90 to 8.74 ml (Table 1). Background CO₂ derived from Iceland spar calcite
214 ranged from 0.50 to 0.76 pMC which is below the long-term ¹⁴C background for these molecular sieve
215 cartridges (1.0 ± 0.5 (SD) pMC based on n = 15 measurements between 2010 and 2015 processed
216 using an earlier EGM4-based sampling kit; Hardie et al. 2005; Garnett et al. 2019). Both ¹⁴C
217 measurements of CO₂ derived from FIRI Belfast cellulose were within measurement uncertainty (<2

218 σ) of the consensus value. For the three TIRI barley mash CO₂ standards, two were within
219 measurements uncertainty ($<2\sigma$) of the consensus value, and one was slightly outside (2.3σ).
220 However, the latter had a CO₂ volume below that currently recommended by the lab for molecular
221 sieve CO₂ samples (Garnett et al. 2019). With one exception, the $\delta^{13}\text{C}$ values for the standards were
222 within measurement uncertainty ($<2\sigma$) of the reference value.

223 The 9 samples of respired CO₂ collected from the replicated soil incubations spanned from $89.83 \pm$
224 0.42 to 90.98 ± 0.40 pMC, a range of 1.15 pMC (Table 2). Samples collected using the Mini kit had an
225 average ¹⁴C content of 90.53 ± 0.47 (SD) pMC which was very similar to the samples collected using
226 the EGM4 system (average 90.63 ± 0.40 (SD) pMC). The $\delta^{13}\text{C}$ values of respired CO₂ were also in close
227 agreement, with averages of -25.3 ± 0.2 (SD) and -25.2 ± 0.5 (SD) for the Mini kit and EGM4 system,
228 respectively. For the 3 incubation vessels that were sampled using both systems, ¹⁴C measurements
229 differed by between 0.1 and 0.55 pMC, and therefore, measurements on the same sample by the
230 two sampling systems were easily within measurement uncertainty. A 2-sample t-test confirmed that
231 there were no statistical differences between the Mini-kit and EGM4 system for both ¹⁴C ($p = 0.752$)
232 and $\delta^{13}\text{C}$ ($p = 0.591$) measurements.

233

234 DISCUSSION

235 Performance of the Mini kit for collecting CO₂ samples for radiocarbon analysis

236 The molecular sieve cartridges used in the Mini kit have previously been shown to perform reliably
237 when used with an earlier sampling kit built around an EGM4 IRGA (Hardie et al. 2005; Garnett et al.
238 2013, 2019). The ¹⁴C results of standard gases when collected using the Mini kit are at least as good
239 and potentially better. For example, the long-term background for the molecular sieve cartridges
240 using the EGM4 sampling kit is 1.0 ± 0.5 pMC (Garnett et al. 2019) but all three background standards
241 tested using the Mini kit had lower ¹⁴C contents (0.50 to 0.76 pMC). This lower background may
242 reflect the simpler design of the Mini kit, with fewer connections and smaller internal surface area,
243 reducing the opportunity for leaks and carry-over of CO₂ between samples (the results in Table 1
244 confirm the absence of significant memory effects as previously reported for this molecular sieve
245 cartridge; Garnett et al. 2013, 2019). Although a ¹⁴C result for one TIRI barley mash CO₂ standard was
246 just outside the 2σ measurement uncertainty, this was for a CO₂ volume below the minimum
247 recommended for these molecular sieve cartridges (3 ml; Garnett et al. 2019) and may reflect the
248 performance of the cartridges rather than the sampling kit.

249 We performed a soil incubation study to provide a test of the Mini kit for the collection of CO₂ under
250 conditions that are more representative of those for which the kit is designed. Use of a homogenised
251 compost in a sealed incubation vessel allowed us to reduce the effects of natural variability that
252 might have been more significant if we had chosen to perform the test using field-based chambers.
253 Additionally, the peat-based compost produced CO₂ that was ¹⁴C-depleted relative to the
254 contemporary atmosphere, and therefore, made our test sensitive to contamination from
255 atmospheric CO₂. The results from this test strongly support the reliability of the Mini kit since i)
256 there was no significant difference in ¹⁴C concentration between samples collected with the Mini kit
257 and those from an established EGM4-based system, and ii) all nine CO₂ samples had ¹⁴C contents that
258 agreed within 2σ measurement uncertainty.

259

260 Measurement of CO₂ concentration and requirements for collection of ¹⁴CO₂ samples

261 The ability to monitor CO₂ concentrations in molecular sieve sampling systems is extremely useful
262 for several reasons. Firstly, it provides key information to estimate whether enough CO₂ has been
263 collected for the ¹⁴C and ¹³C measurements. We use two approaches to estimating the volume of CO₂
264 collected during sampling. In situations where CO₂ is recovered from a chamber or vessel of known
265 volume, we use:

$$266 \quad V = ((C_s - C_e) / 1 \times 10^6) \times V_c \quad (1)$$

267 Where V is the volume (ml) of sample CO₂ trapped in the molecular sieve cartridge (ml), V_c is the
268 chamber volume (ml), and C_s and C_e are the measured CO₂ concentrations (ppm) in the chamber at
269 the start and end of the CO₂ collection, respectively. If substantial CO₂ production in the chamber is
270 still occurring (e.g. due to respiration or evasion), this calculation would provide a minimum estimate
271 for CO₂ collected.

272 When sampling from an unenclosed volume (e.g. when collecting atmospheric CO₂) the volume of
273 CO₂ trapped can be calculated using:

$$274 \quad V = (C_a / 1 \times 10^6) \times F \times T \quad (2)$$

275 Where C_a is the average CO₂ concentration (ppm) measured during sampling time T (min), assuming
276 a flow rate F (ml/min).

277 The measurement of CO₂ concentration of the gas being sampled is common to both approaches,
278 and hence the requirement for an instrument to measure CO₂ concentration. However, the
279 molecular sieve cartridges that we use typically have an operating range in respect to the volume of
280 CO₂ in the order of 3 ml to 10 ml (the latter being the volume at which the molecular sieve starts to
281 become saturated and not trap all the CO₂ in the gas stream). Inaccuracies in measurements of CO₂
282 concentration of ca. 100 ppm usually make little difference to the estimates of CO₂ volume trapped
283 given typical chamber volumes (e.g. 1 to 5 L). Our results show that the performance of the SprintIR®-
284 W CO₂ sensor in the Mini kit is more than adequate for ensuring that enough sample CO₂ has been
285 collected (our results are also consistent with the manufacturer's specifications for the SprintIR®-W
286 CO₂ sensor of an accuracy of ±70 ppm + 5% of reading; www.gassensing.co.uk).

287 Measurement of CO₂ concentration can also be useful to ensure that scrubbing with soda lime has
288 removed the contaminating influence of atmospheric CO₂ from chambers and incubation vessels,
289 prior to sample CO₂ build-up. The high sensitivity of IRGAs is an advantage here because they provide
290 the ability to detect in the order of microlitres of CO₂ remaining in, for example, a 1 L vessel, which
291 would not be detectable using the SprintIR®-W CO₂ sensor. However, in most situations, such as in
292 sampling soil respiration or aquatic CO₂ evasion, CO₂ accumulation inside the chambers would
293 continue throughout the CO₂ scrubbing phase, and therefore, the chamber CO₂ concentration would
294 never reach 0 ppm anyway. A more suitable approach to ensuring complete removal of atmospheric
295 CO₂ from a chamber is to quantify the volume of air scrubbed, in terms of the equivalent chamber
296 volumes (e.g. Kwon et al. 2019), which is based on pump speed and not CO₂ concentration (as a rule
297 we aim to scrub a volume equivalent to at least 5 times the chamber volume).

298 An instrument that measures CO₂ concentration is useful in a molecular sieve sampling kit for leak
299 testing. Leak testing can be performed by removing all the CO₂ in a sampling system (e.g. Mini kit
300 and chambers) when set in a closed loop configuration (Palonen 2015). Once the CO₂ in the system
301 has been removed (or at least reduced significantly below that of the surrounding air), by continuing
302 to pump the air inside the system, but not through soda lime or molecular sieve, any leaks should be
303 detectable from the ingress of atmospheric CO₂. Clearly detection of leaks will depend on the rate of

304 atmospheric ingress and the sensitivity of the instrument performing the CO₂ measurements, with
305 the higher sensitivity of an IRGA being an advantage. To compensate for the lower sensitivity of the
306 Mini kit CO₂ sensor, leak testing can be performed over a longer period. We also periodically perform
307 leak tests by coupling the Mini kit to an IRGA.

308 In our view, the lower sensitivity of the Mini kit's CO₂ sensor compared to an IRGA is not a major
309 disadvantage and is more than compensated by advantages of increased portability, lower power
310 requirements and cost.

311

312 **Expanding the potential for ¹⁴CO₂ methodology in experiments and around the world**

313 ¹⁴CO₂ approaches offer unique insight into soil C cycling rates and partitioning of biogeochemical
314 fluxes of C (Levin and Hessheimer 2000; Wotte et al. 2017b), however, current collection
315 methodologies limit their potential going forward. The expanded use of ¹⁴CO₂ approaches calls for
316 increased replicates to detect statistically meaningful effects (Gavazov et al. 2018; Hartley et al. 2012;
317 Street et al. 2020). The size and cost of the Mini kit will allow ¹⁴CO₂ methods to rise to the challenge
318 of increased sampling intensity for two reasons: (1) its low cost means that multiple systems can be
319 used in tandem (potentially measuring from control and treatment in parallel) and (2) the reduced
320 size allows for ease of use in more challenging environments. Additionally, the system requires little
321 maintenance other than renewal of chemical absorbents and the battery (daily/weekly, depending
322 on use). In the Arctic, the research community is calling for an expansion of field study locations to
323 more generally understand the response of these carbon-rich ecosystems to climate change
324 (Metcalf et al. 2018). A low cost, low tech system will enable researchers to answer this call when
325 ¹⁴CO₂ methodologies are appropriate.

326

327 **CONCLUSIONS**

328 We conclude that the Mini kit molecular sieve sampling system is reliable for the collection of CO₂
329 samples for ¹⁴C analysis and has a performance at least as good as an established system (Hardie et
330 al. 2005; Garnett et al. 2019). The Mini kit is highly portable (the pump/sensor unit including battery
331 weighs only 650 g and can be contained within an 18 cm x 12 cm x 8 cm enclosure, such as a
332 waterproof sandwich box) and has low power demands (we have found a single PP9 battery to
333 provide at least 10 hours continuous use, potentially allowing for the collection of many samples per
334 day) making it particularly useful for sampling in remote and inaccessible locations. The Mini kit is
335 also relatively inexpensive with the pump/sensor unit costing ca. UK £300 and negating the need for
336 a much more expensive IRGA. Recently, Metcalfe et al. (2018) highlighted the poor spatial
337 distribution of ecological studies in the Arctic, showing the bias towards sampling in relatively
338 accessible locations. The Mini kit can aid efforts to overcome the challenges of field sampling of CO₂
339 for ¹⁴C analysis and help address calls to reduce spatial bias in ecological studies through increased
340 sampling of remote and inaccessible locations.

341

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347

348 REFERENCES

349 Billett MF, Garnett MH, Harvey F (2007) UK peatland streams release old carbon dioxide to the
350 atmosphere and young dissolved organic carbon to rivers. *Geophysical Research Letters* 34: L23401.
351 doi:10.1029/2007GL031797.

352 Boaretto E, Bryant C, Carmi I, Cook G, Gulliksen S, Harkness D, Heinemeier J, McClure J, McGee E,
353 Naysmith P, Possnert G, Scott M, van der Plicht H, van Strydonck M (2002) Summary findings of the
354 fourth international radiocarbon intercomparison (FIRI)(1998–2001). *Journal of Quaternary Science*
355 17(7): 633-637. doi:10.1002/jqs.702

356 Bol RA, Harkness DD (1995) The use of zeolite molecular sieves for trapping low concentrations of
357 CO₂ from environmental atmospheres. *Radiocarbon* 37(2): 643-647.
358 doi.org/10.1017/S0033822200031155

359 Breck D (1974) *Zeolite Molecular Sieves: Structure, Chemistry and Use*. John Wiley & Sons Inc., New
360 York

361 Campeau A, Bishop K, Amvrosiadi N, Billett MF, Garnett MH, Laudon H, Öquist MG, Wallin MB (2019)
362 Current forest carbon fixation fuels stream CO₂ emissions. *Nature Communications* 10(1): 1876.
363 10.1038/s41467-019-09922-3

364 Dean JF, Meisel OH, Martyn Rosco M, Marchesini LB, Garnett MH, Lenderink H, van Logtestijn R,
365 Borges AV, Bouillon S, Lambert T, Röckmann T, Maximov T, Petrov R, Karsanaev S, Aerts R, van
366 Huissteden J, Vonk JE, Dolman AJ (2020) East Siberian Arctic inland waters emit mostly contemporary
367 carbon. *Nature Communications* 11(1): 1627. 10.1038/s41467-020-15511-6

368 Garnett MH, Murray C (2013) Processing of CO₂ samples collected using zeolite molecular sieve for
369 ¹⁴C analysis at the NERC Radiocarbon Facility (East Kilbride, UK). *Radiocarbon* 55(2-3): 410-415.
370 doi.org/10.1017/S0033822200057532

371 Garnett MH, Newton J-A, Ascough PL (2019) Advances in the radiocarbon analysis of carbon dioxide
372 at the NERC Radiocarbon Facility (East Kilbride) using molecular sieve cartridges. *Radiocarbon* 61(6):
373 1855-1865. 10.1017/RDC.2019.86

374 Gaudinski JB, Trumbore SE, Davidson EA, Zheng S (2000) Soil carbon cycling in a temperate forest:
375 radiocarbon-based estimates of residence times, sequestration rates and partitioning of fluxes.
376 *Biogeochemistry* 51: 33-69. doi.org/10.1023/A:1006301010014

377 Gavazov K, Albrecht R, Buttler A, Dorrepaal E, Garnett MH, Gogo S, Hagedorn F, Mills RTE, Robroek
378 BJM, Bragazza L (2018) Vascular plant-mediated controls on atmospheric carbon assimilation and
379 peat carbon decomposition under climate change. *Global Change Biology* 24(9): 3911-3921.
380 doi:10.1111/gcb.14140

381 Gulliksen S, Scott M (1995) Report of the TIRI workshop, Saturday 13 August, 1994. *Radiocarbon*
382 37(2): 820-821. doi.org/10.1017/S0033822200031404

383 Hämäläinen K, Fritze H, Jungner H, Karhu K, Oinonen M, Sonninen E, Spetz P, Tuomi M, Vanhala P,
384 Liski J (2010) Molecular sieve sampling of CO₂ from decomposition of soil organic matter for AMS

385 radiocarbon measurements. *Nuclear Instruments and Methods in Physics Research Section B: Beam*
386 *Interactions with Materials and Atoms* 268(7): 1067-1069. doi.org/10.1016/j.nimb.2009.10.099

387 Hardie SML, Garnett MH, Fallick AE, Rowland AP, Ostle NJ (2005) Carbon dioxide capture using a
388 zeolite molecular sieve sampling system for isotopic studies (¹³C and ¹⁴C) of respiration. *Radiocarbon*
389 47(3): 441-451. doi.org/10.1017/S0033822200035220

390 Hartley IP, Garnett MH, Sommerkorn M, Hopkins DW, Fletcher BJ, Sloan VL, Phoenix GK, Wookey PA
391 (2012) A potential loss of carbon associated with greater plant growth in the European Arctic. *Nature*
392 *Climate Change* 2: 875-879. DOI: 10.1038/NCLIMATE1575

393 Kwon MJ, Natali SM, Hicks Pries CE, Schuur EAG, Steinhof A, Crummer KG, Zimov N, Zimov SA,
394 Heimann M, Kolle O, Göckede M (2019) Drainage enhances modern soil carbon contribution but
395 reduces old soil carbon contribution to ecosystem respiration in tundra ecosystems. *Global Change*
396 *Biology* 25(4): 1315-1325. 10.1111/gcb.14578

397 Levin I, Hesshaimer V (2000) Radiocarbon - A unique tracer of global carbon cycle dynamics.
398 *Radiocarbon* 42(1): 69-80. doi.org/10.1017/S0033822200053066

399 Major I, Haszpra L, Rinyu L, Futó I, Bihari Á, Hammer S, Jull AJT, Molnár M (2018) Temporal variation
400 of atmospheric fossil and modern CO₂ excess at a central European rural tower station between 2008
401 and 2014. *Radiocarbon* 60(5): 1285-1299. 10.1017/RDC.2018.79

402 Metcalfe DB, Hermans TDG, Ahlstrand J, Becker M, Berggren M, Björk RG, Björkman MP, Blok D,
403 Chaudhary N, Chisholm C, Classen AT, Hasselquist NJ, Jonsson M, Kristensen JA, Kumordzi BB, Lee H,
404 Mayor JR, Prevéy J, Pantazatou K, Rousk J, Sponseller RA, Sundqvist MK, Tang J, Uddling J, Wallin G,
405 Zhang W, Ahlström A, Tenenbaum DE, Abdi AM (2018) Patchy field sampling biases understanding
406 of climate change impacts across the Arctic. *Nature Ecology & Evolution* 2(9): 1443-1448.
407 10.1038/s41559-018-0612-5

408 Molnár M, Haszpra L, Svingor É, Major I, Svetlik I (2010) Atmospheric fossil fuel CO₂ measurement
409 using a field unit in a central European city during the winter of 2008/09. *Radiocarbon* 52(2): 835-
410 845. 10.1017/S0033822200045859

411 Palonen V (2015) A portable molecular-sieve-based CO₂ sampling system for radiocarbon
412 measurements. *Review of Scientific Instruments* 86: 125101. doi.org/10.1063/1.4936291

413 Slota P, Jull AJT, Linick T, Toolin LJ (1987) Preparation of small samples for ¹⁴C accelerator targets by
414 catalytic reduction of CO. *Radiocarbon* 29(2): 303-306. doi.org/10.1017/S0033822200056988

415 Street LE, Garnett MH, Subke J-A, Baxter R, Dean JF, Wookey PA (2020) Plant carbon allocation drives
416 turnover of old soil organic matter in permafrost tundra soils. *Global Change Biology* 26(8): 4559-
417 4571. 10.1111/gcb.15134

418 Stuiver M, Polach HA (1977) Reporting of ¹⁴C data. *Radiocarbon* 19(3): 355-363.
419 doi.org/10.1017/S0033822200003672

420 Wotte A, Wischhöfer P, Wacker L, Rethemeyer J (2017a) ¹⁴CO₂ analysis of soil gas: Evaluation of
421 sample size limits and sampling devices. *Nuclear Instruments and Methods in Physics Research*
422 *Section B: Beam Interactions with Materials and Atoms* 413: 51-56.
423 doi.org/10.1016/j.nimb.2017.10.009

424 Wotte A, Wordell-Dietrich P, Wacker L, Don A, Rethemeyer J (2017b) ¹⁴CO₂ processing using an
425 improved and robust molecular sieve cartridge. *Nuclear Instruments and Methods in Physics*

426 Research Section B: Beam Interactions with Materials and Atoms 400: 65-73.
427 doi.org/10.1016/j.nimb.2017.04.019

428 Zhou W, Niu Z, Wu S, Xiong X, Hou Y, Wang P, Feng T, Cheng P, Du H, Lu X, An Z, Burr GS, Zhu Y (2020)
429 Fossil fuel CO₂ traced by radiocarbon in fifteen Chinese cities. Science of The Total Environment 729:
430 138639. doi.org/10.1016/j.scitotenv.2020.138639

431

432 **SUPPLEMENTARY**

433 List of components, schematic of electronics, Arduino code and sampling setups

434 Table 1 Results for carbon dioxide derived from radiocarbon reference materials collected using the
 435 Mini kit sampling system. Reference values for radiocarbon standards: ^aGulliksen and Scott (1995),
 436 ^bBoaretto et al. (2002). STP = Standard temperature and pressure. Mean pMC ± SD: 116.30 ± 1.12
 437 (TIRI barley mash) and 0.65 ± 0.13 (Iceland spar calcite).

438

Publication code (SUERC-)	Source of CO ₂ standard	Reference pMC ± 1 σ	Reference δ ¹³ C ± 0.3 ‰	Measured pMC ± 1 σ	Measured δ ¹³ C ± 0.3 ‰	Sample volume (ml STP)
74593	TIRI barley mash	116.35 ± 0.0084 ^a	-26.8	116.35 ± 0.54	-26.7	3.06
74594	Iceland spar calcite	Background	+2.4	0.68 ± 0.01	+2.2	2.94
74529	TIRI barley mash	116.35 ± 0.0084 ^a	-26.8	117.39 ± 0.52	-26.2	4.43
74543	Iceland spar calcite	Background	+2.4	0.50 ± 0.01	+2.3	8.74
74549	FIRI Belfast cellulose	57.22 ± 0.04 ^b	-23.6	57.42 ± 0.34	-23.8	7.57
84290	TIRI barley mash	116.35 ± 0.0084 ^a	-26.8	115.15 ± 0.53	-27.0	2.90
84291	FIRI Belfast cellulose	57.22 ± 0.04 ^b	-23.6	56.68 ± 0.33	-23.8	4.74
84292	Iceland spar calcite	Background	+2.4	0.76 ± 0.01	+1.8	2.81

439

440 Table 2 Carbon isotopic composition of respired CO₂ from replicated incubations of a peat-based
 441 compost. Samples were collected using the new Mini kit sampling system and the established
 442 EGM4-based system described by Hardie et al. (2005). Incubation vessels marked (^a) were sampled
 443 using both systems. STP = Standard temperature and pressure. Mean pMC ± SD: 90.53 ± 0.47 (Mini
 444 kit) and 90.63 ± 0.40 (EGM4 system).

445

Publication code (SUERC-)	Soil incubation vessel	Sampling system	Measured pMC ± 1 σ	Measured δ ¹³ C ± 0.3 ‰	Sample volume (ml STP)
85081	1	Mini kit	90.55 ± 0.40	-25.3	5.97
85085	2	EGM4 system	90.93 ± 0.40	-25.4	6.17
85086	3	Mini kit	89.83 ± 0.42	-25.6	5.92
85087	4	EGM4 system	90.72 ± 0.40	-25.5	6.19
85088	5	Mini kit	90.98 ± 0.40	-25.4	5.93
85089	6	EGM4 system	90.82 ± 0.42	-25.3	6.01
85090	2 ^a	Mini kit	90.38 ± 0.42	-25.3	6.00
85091	3 ^a	EGM4 system	90.04 ± 0.42	-24.5	5.81
85095	6 ^a	Mini kit	90.92 ± 0.42	-25.0	5.64

446

447 **Figure captions**

448 Figure 1 Mini kit for collecting carbon dioxide for radiocarbon analysis. Photographs show (a) the
449 field deployment of the system to sample soil-respired CO₂ and (b) an internal view of the CO₂
450 sensor/pump unit. Schematic (c) showing the connections to a respiration chamber. Note that clips
451 are used to direct the gas flow through either the soda lime or molecular sieve cartridges and that
452 an empty cartridge replaces the molecular sieve trap when monitoring CO₂ build-up in the
453 chamber. Red arrows indicate the direction of gas flow.

454

455 Figure 2 Carbon dioxide concentration measurements made on the same gas stream using the
456 SprintIR®-W CO₂ sensor of the Mini kit and the EGM4 IRGA used in the Hardie et al. (2005) sampling
457 system. The source gas was cycled three times in the order: outside air (A), pure nitrogen (B), a 10 L
458 foil gas bag containing lab air (ca. 790 ppm; C), outside air passed through soda lime to remove CO₂
459 (D) and a second 10 L foil gas bag containing an elevated CO₂ concentration (ca. 2200 ppm; E). An
460 EGM5 IRGA was used to provide an independent measurement of CO₂ concentration in the gas
461 bags.

462

463 Figure 3 Field collection of respired CO₂ from a grassland soil using a closed chamber and the Mini
464 kit sampling system. The graph shows the CO₂ concentration of the chamber measured by the
465 SprintIR®-W CO₂ sensor of the Mini kit and an EGM5 IRGA during scrubbing (removal of
466 atmospheric CO₂), CO₂ build-up and CO₂ collection. Note that auto-calibration of the EGM5 every
467 30 minutes removed CO₂ from the chamber causing small step changes in chamber CO₂
468 concentration. The flow rate of the Mini kit sampling system was monitored using the flow sensor
469 of the EGM5 (the EGM5 internal pump was disabled).

470

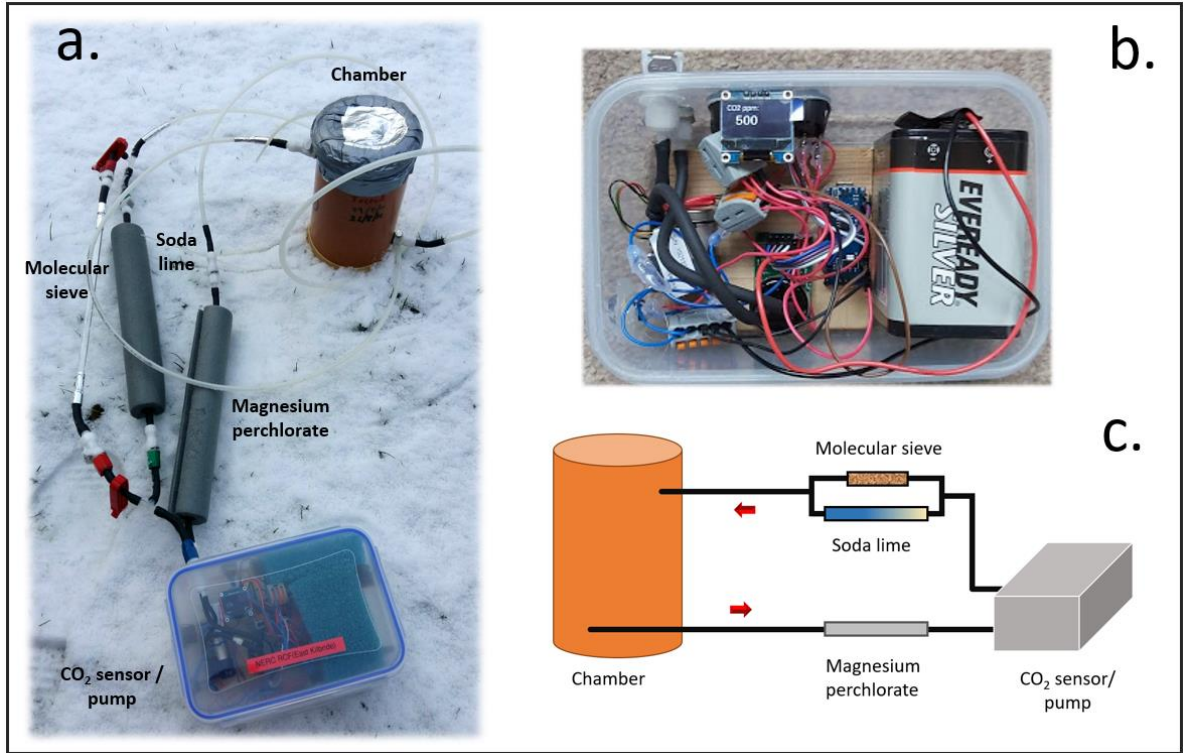
471 Figure 1

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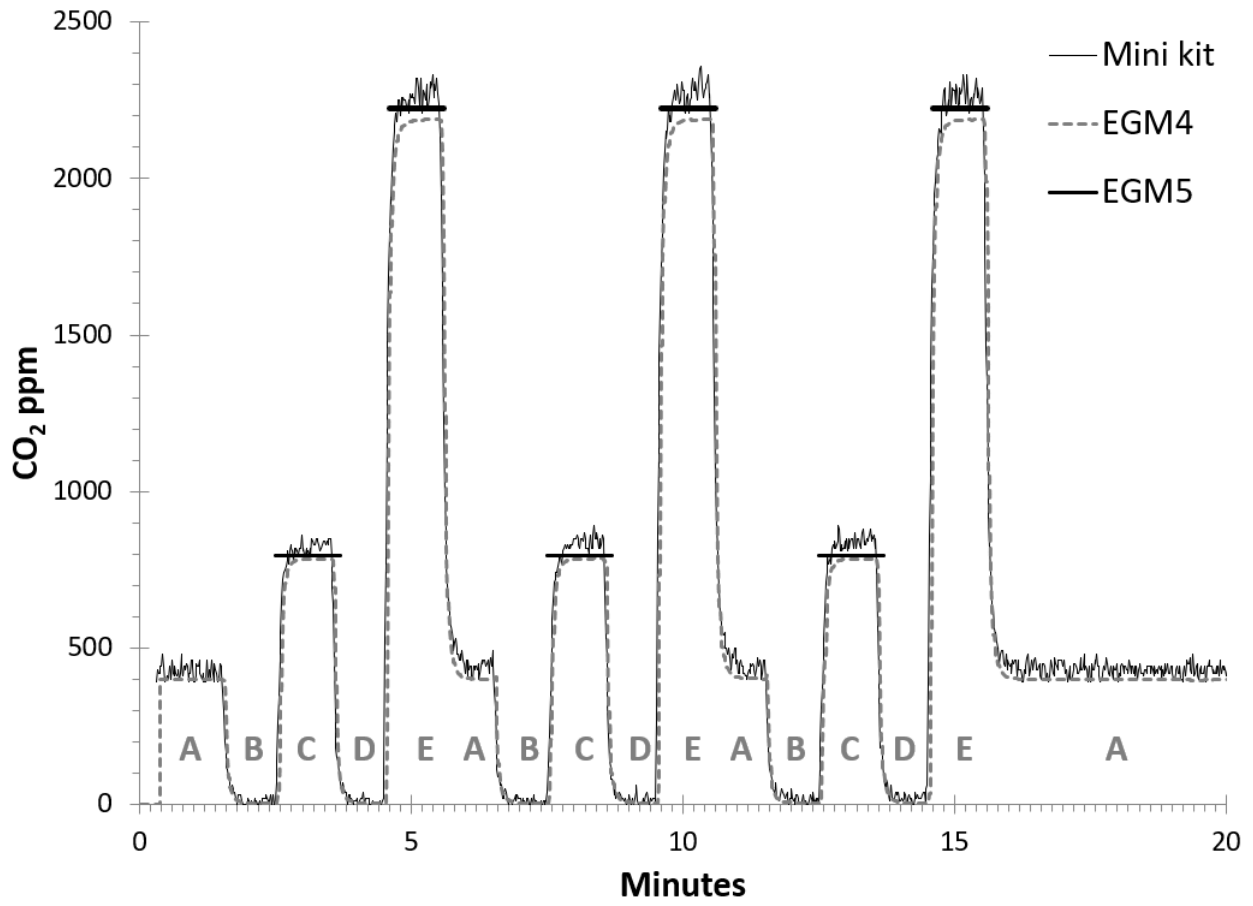
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483 Figure 2

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485 Figure 3

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