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1 **A passive sampling method for radiocarbon analysis of atmospheric CO<sub>2</sub> using**  
2 **molecular sieve**

3

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16

17 **Abstract**

18

19 Radiocarbon (<sup>14</sup>C) analysis of atmospheric CO<sub>2</sub> can provide information on CO<sub>2</sub>

20 sources and is potentially valuable for validating inventories of fossil fuel-derived

21 CO<sub>2</sub> emissions to the atmosphere. We tested zeolite molecular sieve cartridges, in

22 both field and laboratory experiments, for passively collecting atmospheric CO<sub>2</sub>.

23 Cartridges were exposed to the free atmosphere in two configurations which

24 controlled CO<sub>2</sub> trapping rate, allowing collection of sufficient CO<sub>2</sub> in between 1.5 to

25 10 months at current levels. <sup>14</sup>C results for passive samples were within measurement

26 uncertainty of samples collected using a pump-based system, showing that the method  
27 collected samples with  $^{14}\text{C}$  contents representative of the atmosphere.  $\delta^{13}\text{C}$  analysis  
28 confirmed that the cartridges collected representative  $\text{CO}_2$  samples, however,  
29 fractionation during passive trapping means that  $\delta^{13}\text{C}$  values need to be adjusted by an  
30 amount which we have quantified. Trapping rate was proportional to atmospheric  $\text{CO}_2$   
31 concentration, and was not affected by exposure time unless this exceeded a  
32 threshold. Passive sampling using molecular sieve cartridges provides an easy and  
33 reliable method to collect atmospheric  $\text{CO}_2$  for  $^{14}\text{C}$  analysis.

34

35 *Keywords:* Atmospheric  $\text{CO}_2$ , Radiocarbon, Passive sampling, Molecular sieve.

36

## 37 **1. Introduction**

38

39 The radiocarbon ( $^{14}\text{C}$ ) concentration of atmospheric  $\text{CO}_2$  can provide valuable  
40 information on the sources of this dominant greenhouse gas and its rate of exchange  
41 between the atmosphere and other components of the carbon cycle (Levin and  
42 Hesshaimer, 2000). For example, since  $^{14}\text{C}$  radioactively decays, fuels derived from  
43 ancient fossil sources are  $^{14}\text{C}$ -free which contrasts strongly with contemporary  
44 atmospheric  $\text{CO}_2$ . This difference has been used to assess the contribution of fossil  
45 fuel-derived  $\text{CO}_2$  from industrial activities to both the local (e.g. Baxter and Harkness,  
46 1975) and regional/global (Levin et al., 2008) atmosphere, and to validate changes in  
47 fossil fuel  $\text{CO}_2$  emissions under the Kyoto protocol (Levin and Rödenbeck, 2008).  
48 Marquis and Tans (2008) called for a global increase in the network of  $\text{CO}_2$   
49 observation stations with simultaneous monitoring of isotopes, including  $^{14}\text{C}$ , to  
50 assess regional changes in greenhouse gas emissions. Atmospheric  $^{14}\text{CO}_2$

51 measurements have also been used to monitor emissions around nuclear facilities (e.g.  
52 Povinec et al., 2009).

53

54  $^{14}\text{C}$  determination typically requires a few millilitres of  $\text{CO}_2$  if the isotope  
55 measurement is performed by accelerator mass spectrometry (AMS). At current  
56 concentrations, several litres of air are required. Suitable samples can be collected  
57 using flasks or gas sample bags, and the  $\text{CO}_2$  purified using cryogenic trapping.

58 However, this method will provide a sample representative of only one point in time,  
59 whereas it may be more relevant to collect samples representative of longer periods.

60 This can be achieved by slowly pumping air through a medium which extracts the  
61  $\text{CO}_2$ , for example, using cryogenic trapping or an absorbent such as molecular sieve  
62 (e.g. Hardie et al., 2005). An alternative is to make use of passive samplers.

63

64 Passive  $\text{CO}_2$  samplers rely solely on diffusion for the  $\text{CO}_2$  to be transported to an  
65 absorbent. They are therefore highly preferable in many situations since they do not  
66 require an external energy supply and, due to having no moving mechanical parts, are  
67 very reliable; passive samplers simply need to be deployed for the required period of  
68 time and returned to the laboratory for analysis.

69

70 Several absorbents have been used in passive  $\text{CO}_2$  samplers including hydroxides and  
71 molecular sieve, however, few studies have used the passive sampling approach for  
72 collecting samples for  $^{14}\text{CO}_2$  analysis. Cooper et al. (1998) provide one example of  
73 passive sampling for  $^{14}\text{CO}_2$  measurement using hydroxides. However, their samplers  
74 were designed for measuring  $^{14}\text{C}$  concentrations much higher than natural abundance  
75 (for monitoring nuclear facilities). Davidson (1995) noted that considerable care must

76 be taken using hydroxide for the absorbent since even fresh hydroxide may contain a  
77 significant quantity of CO<sub>2</sub> (leading to sample contamination). Additionally,  
78 hydroxides are potentially harmful, requiring care during deployment.

79

80 We have developed a passive sampling approach utilising Type 13X zeolite molecular  
81 sieve. Zeolite molecular sieve is an extremely effective CO<sub>2</sub> absorbent that does not  
82 suffer from many of the disadvantages that affect hydroxides. The technique employs  
83 exactly the same molecular sieve cartridge (MSC) that was tested by Hardie et al.  
84 (2005) and found not to suffer from fractionation, contamination or sample carry-over  
85 effects when used with a pump-based sampling system. Application of the MSC in  
86 passive sampling form has already been successfully tested for trapping samples of  
87 soil respired CO<sub>2</sub> for <sup>14</sup>C measurement (Garnett et al., 2009). However, the CO<sub>2</sub>  
88 concentrations involved in collecting soil respired CO<sub>2</sub> were far higher than those  
89 likely to be encountered in the atmosphere.

90

91 In the present study, our investigation focused around determining 1. whether passive  
92 sampling trapped CO<sub>2</sub> on the sieve at a rate which was representative of the  
93 atmospheric CO<sub>2</sub> concentration, no matter what the sampling period, and 2. if the CO<sub>2</sub>  
94 recovered from the passive sampler had an isotopic composition representative of the  
95 atmosphere being sampled.

96

## 97 **2. Materials and methods**

98

### 99 *2.1. Molecular sieve cartridge (MSC) design and procedures*

100

101 We employed the MSC previously described by Hardie et al. (2005) and Garnett et al.  
102 (2009), and illustrated schematically in Fig. 1. The cartridge was composed of quartz  
103 glass tubing containing ~3-4 g of 13X zeolite molecular sieve (1/16" pellets, BDH,  
104 UK) held within a central chamber by quartz wool. The cartridge was sealed by two  
105 auto-shutoff Quick Couplings (Colder Products Company, USA) attached via short  
106 lengths of tubing (Tygon, Fisher, UK). When not mated to other couplings, the  
107 couplings on the MSC automatically sealed. When not being used for sampling, a clip  
108 (WeLoc<sup>®</sup>, Scandinavia Direct, UK) was placed across the tubing to form an additional  
109 seal. During sampling, the molecular sieve was exposed to atmosphere by attaching  
110 another coupling to the MSC coupling, opening the auto-shutoff valve. This additional  
111 coupling was open to atmosphere via a tubular hydrophobic filter (Accurel PP V8/2  
112 HF, Membrana GmbH, Germany; Gut et al., 1998); air was free to pass from the  
113 atmosphere through the filter into the MSC, however, the filter prevented entry of  
114 liquid water. Prior to sampling, each MSC was charged by heating (500 °C) under  
115 vacuum ( $10^{-3}$  mB) to remove residual moisture or CO<sub>2</sub> trapped on the sieve. When  
116 cool, the MSC was filled to slightly above atmospheric pressure with high purity N<sub>2</sub>.

117

## 118 *2.2. Field experiment*

119

120 We employed the MSCs in two sampling configurations. For the ‘one opening’  
121 configuration the sieve was exposed to the atmosphere through the narrow end of the  
122 cartridge, by attaching a single coupling (with filter). For the ‘two openings’  
123 configuration, the sieve was exposed at both ends by attaching two couplings.

124

125 During sampling all MSCs were protected inside a length of plastic drain pipe (110  
126 mm diameter, 600 mm length) which was fully open at both ends ensuring that all  
127 samplers were exposed to the same atmosphere. Sampling was performed from a first  
128 floor window ledge in a suburban site to the south of Glasgow, UK (55°46'N,  
129 4°18'W), at a location away from large local sources of CO<sub>2</sub> and approximately 20 m  
130 from the nearest road. The experiment to test the 'one opening' configuration ran  
131 from 13<sup>th</sup> June 2007 until 2<sup>nd</sup> April 2008, and the 'two openings' mode was tested  
132 between 3<sup>rd</sup> September 2007 and 18<sup>th</sup> February 2008.

133

134 We employed a sampling design based on Bertoni et al. (2004) that allows a test that  
135 the MSCs trap representative CO<sub>2</sub> samples at a rate proportional to the environmental  
136 concentration. The design utilises multiple exposures performed simultaneously over  
137 defined units of time. We chose three exposure times; a short, medium and long  
138 period (Fig. 2). At any one time, three MSCs were sampling, one from each of the  
139 short, medium and long sampling periods. If the MSCs were collecting representative  
140 samples then combined results for shorter period samples should equal the results for  
141 the longer period sample that was collected over the same time period (e.g. combined  
142 results from S1 and S2 should equal the result for M1). To test for identical trapping  
143 rates, the recovered CO<sub>2</sub> volumes for shorter period samples are summed, whereas to  
144 test that isotopically identical samples were collected, weighted average values were  
145 determined. Additionally, to test MSCs collected isotopically representative samples  
146 of atmospheric CO<sub>2</sub>, we collected three sets of samples using the pump-based  
147 molecular sieve sampling system (Hardie et al., 2005) at the study site for 1 hour at  
148 the start, middle and end of each experiment.

149

150 2.3. *Additional laboratory experiments*

151

152 In the field, atmospheric CO<sub>2</sub> concentrations and isotopic ratios vary temporally,  
153 making it difficult to determine whether rates of CO<sub>2</sub> collection are proportional to the  
154 CO<sub>2</sub> concentration, and to precisely quantify any isotopic fractionation which occurs.  
155 Therefore, we carried out a laboratory experiment in which MSCs passively sampled  
156 the atmosphere inside a 30 L air-tight plastic barrel; by mounting the outer coupling  
157 (with hydrophobic filter) to the barrel lid, MSCs could be attached to sample the  
158 barrel atmosphere in an identical way to the field sampling. The barrel atmosphere  
159 was adjusted to give three different CO<sub>2</sub> concentrations, and duplicate samples of CO<sub>2</sub>  
160 were concurrently collected by passive sampling. As well as measuring the volume of  
161 CO<sub>2</sub> collected, to determine whether passive sampling caused isotopic fractionation,  
162  $\delta^{13}\text{C}$  values were compared with samples collected by evacuated flask.

163

164 It has been recognized that N<sub>2</sub>O can interfere with mass spectrometer  $\delta^{13}\text{C}$   
165 measurements of atmospheric CO<sub>2</sub> (see Ehleringer, 1991). Godbout et al. (2006)  
166 showed that N<sub>2</sub>O can be trapped by zeolite molecular sieve (5A) and as N<sub>2</sub>O  
167 condenses at a similar temperature to CO<sub>2</sub> it may not be removed during molecular  
168 sieve discharge. Although trace amounts of N<sub>2</sub>O in the atmosphere may only affect  
169  $\delta^{13}\text{C}$  values by 0.23 ‰ (Ehleringer, 1991), the effect could be greater if the  
170 atmosphere being sampled had enhanced N<sub>2</sub>O concentrations, or if MSCs passively  
171 trapped N<sub>2</sub>O at a greater rate than CO<sub>2</sub>. We therefore tested whether N<sub>2</sub>O caused  
172 interference with  $\delta^{13}\text{C}$  measurement in samples of CO<sub>2</sub> collected using MSCs. First,  
173 we set up a method to remove N<sub>2</sub>O from CO<sub>2</sub> samples by passing the gas over Cu  
174 pellets heated to 650 °C (Ehleringer, 1991). We verified that the method removed N<sub>2</sub>O



175 using prepared gases composed of CO<sub>2</sub> of known δ<sup>13</sup>C, mixed with N<sub>2</sub>O. Samples of  
176 CO<sub>2</sub> recovered using the molecular sieve method (including a sample collected  
177 passively) which had previously been analysed for δ<sup>13</sup>C were subjected to the heated  
178 Cu treatment in the same way, and reanalyzed for δ<sup>13</sup>C; a significant positive shift in  
179 δ<sup>13</sup>C would indicate interference from N<sub>2</sub>O in the first measurement.

180

#### 181 *2.4. CO<sub>2</sub> recovery and isotope analysis*

182

183 After sampling, the MSCs were sealed and returned to the NERC Radiocarbon  
184 Facility for CO<sub>2</sub> recovery by heating and cryogenic trapping (see Hardie et al., 2005).  
185 The recovered CO<sub>2</sub> was divided to provide one aliquot of CO<sub>2</sub> for δ<sup>13</sup>C measurement  
186 and another for <sup>14</sup>C analysis. δ<sup>13</sup>C (per mil) relative to Vienna Pee Dee Belemnite (V-  
187 PDB) was determined on an isotope ratio mass spectrometer (VG Optima, Micromass,  
188 UK) using:

189

$$190 \delta^{13}\text{C} (\text{‰}) = [((^{13}\text{C}/^{12}\text{C})_{\text{Sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{V-PDB}}) / (^{13}\text{C}/^{12}\text{C})_{\text{V-PDB}}] \times 1000 \quad \text{Equation 1}$$

191

192 <sup>14</sup>C analysis was performed only on a selection of samples. For these samples, the  
193 second aliquot of CO<sub>2</sub> was reduced to graphite (Slota et al., 1987) and analysed by  
194 AMS at the Scottish Universities Environmental Research Centre (SUERC; Freeman  
195 et al., 2007). To account for mass-dependant fractionation, <sup>14</sup>C results were  
196 normalised to δ<sup>13</sup>C of -25 ‰ and expressed as %modern (the ratio of the sample <sup>14</sup>C  
197 content relative to the Oxalic acid international radiocarbon standard, expressed on a  
198 % basis; Stuiver and Polach, 1977). Following convention, measurement uncertainties  
199 for isotope concentrations are expressed as standard deviations.

200

### 201 3. Results

202

#### 203 3.1. Field experiment, 'One opening' configuration

204

205 When only one opening of the MSC was exposed to the atmosphere, the combined  
206 volumes of CO<sub>2</sub> recovered from short period samples were almost identical to that  
207 recovered from medium period samples (Table 1). For example, the sum of CO<sub>2</sub>  
208 recovered from the first two short period samples (S1+S2) was 4.1 ml, almost  
209 identical to the M1 sample (4.2 ml) trapping CO<sub>2</sub> over the same time period. The sum  
210 of the CO<sub>2</sub> volumes recovered from the two medium period samples was slightly  
211 higher than recovered in the long period sample (Table 1), although overall, there was  
212 a very significant relationship between CO<sub>2</sub> recovered and exposure time (Fig. 3).

213 Average trapping rate using this configuration was 0.029 ml day<sup>-1</sup> (Fig. 3).

214

215 The combined  $\delta^{13}\text{C}$  values for all short period samples were all within measurement  
216 error ( $< 2 \sigma$ ) of the respective longer period sample exposed over the same time  
217 (Table 1). However, all  $\delta^{13}\text{C}$  values collected using passive MSC sampling were about  
218 3-5 ‰ depleted (see Section 4.4. for precise quantification of fractionation caused by  
219 passive sampling) relative to pumped samples (Table 1). The <sup>14</sup>C content of the long-  
220 period sample collected passively was within measurement uncertainty of the pumped  
221 samples collected at the start and end of the experiment (Table 1).

222

#### 223 3.2. Field experiment, 'Two openings' configuration

224

225 Again, the sum of CO<sub>2</sub> collected in short period samples using the ‘two openings’  
226 configuration was very similar to the volumes recovered from the respective medium  
227 period samples (Table 2). However, the summed volume recovered from the medium  
228 period exposures, was considerably higher than that recovered from the long period  
229 sample (Table 2). Thus the correlation between CO<sub>2</sub> recovered and exposure time was  
230 poor compared to the results for the ‘one opening’ configuration (Fig. 3). Average  
231 CO<sub>2</sub> trapping rate for the ‘two openings’ configuration was 0.082 ml per day, but if  
232 results for the long period were excluded, trapping rate increased to 0.114 ml per day,  
233 and the regression passed closer to the origin (Fig. 3).

234

235 Averaged  $\delta^{13}\text{C}$  values for short period samples were within measurement uncertainty  
236 of the results for the respective medium period samples that had been exposed over  
237 the same period (Table 2). However, the  $\delta^{13}\text{C}$  value for the long period sample  
238 differed considerably from the average of the two medium period samples, the former  
239 being more <sup>13</sup>C-enriched than any other  $\delta^{13}\text{C}$  result from passive MSC samples  
240 (Table 2). All  $\delta^{13}\text{C}$  values for passive MSC samples were depleted in <sup>13</sup>C (see Section  
241 4.4. for precise quantification of fractionation caused by passive sampling) compared  
242 to samples collected using the pumped method (by ~ 2 to 5 ‰).

243

244 Of the samples analysed for <sup>14</sup>C content, the average for the two short period samples  
245 was within measurement uncertainty of the relevant medium period sample (Table 2).  
246 All passive MSC <sup>14</sup>C results were within error of the pumped sample collected at the  
247 start of the experiment, however, the pumped sample collected during the middle of  
248 the experiment (day 84) was significantly <sup>14</sup>C-depleted compared to both the first  
249 pumped sample and all the passive MSC samples (Table 2).

250

### 251 3.3. Laboratory experiments

252

253 When the fixed atmospheres inside a sealed 30 L barrel were passively sampled we  
254 found a strong positive linear correlation between trapping rate and CO<sub>2</sub> concentration  
255 of the atmosphere (Fig. 4). The CO<sub>2</sub> collected passively was <sup>13</sup>C-depleted by an  
256 average of 4.16±0.25 ‰ (SD; n=6) relative to the evacuated flask samples. We found  
257 no significant change (<0.4 ‰) in δ<sup>13</sup>C of CO<sub>2</sub> after it had been passed over heated Cu  
258 at 650 °C in all samples of CO<sub>2</sub> collected using molecular sieve that we tested (Table  
259 3). However, δ<sup>13</sup>C of a sample of soil respired CO<sub>2</sub> collected using an evacuated flask  
260 changed significantly from -25.9 to -25.3 following Cu treatment.

261

## 262 4. Discussion

263

### 264 4.1. Rate of CO<sub>2</sub> trapping

265

266 The results of the laboratory experiment indicate a very high correlation between rate  
267 of CO<sub>2</sub> trapping and CO<sub>2</sub> concentration of the atmosphere to which the MSCs were  
268 exposed (Fig. 4). This relationship is a prerequisite for representative sampling and  
269 was expected based on theoretical calculations using Fick's Law (Bertoni et al.,  
270 2004):

271

$$272 \quad C_i = (Q_i \times L) / (S \times t \times D_i)$$

*Equation 2*

273

274 where  $C_i$  represents the CO<sub>2</sub> concentration of the atmosphere being sampled,  $Q_i$  the  
275 volume of CO<sub>2</sub> trapped during time  $t$ ,  $D_i$  is the diffusion coefficient of CO<sub>2</sub> in air, and  
276  $L$  and  $S$  are the length and cross-sectional area of the entire sampling probe (between  
277 mid points of gas inlet and molecular sieve). As shown in Fig. 4, the theoretical  
278 relationship between trap rate and atmospheric CO<sub>2</sub> concentration predicted by Fick's  
279 Law is almost identical to that from our laboratory experiment. Indeed Bertoni et al.  
280 (2004) specifically developed passive samplers to estimate atmospheric CO<sub>2</sub>  
281 concentration from trap rate (using Ba(OH)<sub>2</sub> as the absorbent).

282

283 To complete our laboratory tests within an acceptable time, CO<sub>2</sub> concentrations inside  
284 the barrel were considerably greater than in the free atmosphere. However, the  
285 relationship between trap rate and CO<sub>2</sub> concentration should be equally valid in  
286 atmospheres of lower CO<sub>2</sub> concentration. Indeed, using equation 2 and the average  
287 trapping rate for samples collected using the 'one opening' configuration of the MSCs  
288 in the field tests (0.029 ml day<sup>-1</sup>) gives an atmospheric CO<sub>2</sub> concentration of ~460  
289 ppm. This value is only slightly higher than direct measurements of CO<sub>2</sub>  
290 concentration measured over the sampling period using an infra red gas analyser  
291 (range 368-411 ppm), and also implies that other factors (e.g. meteorological  
292 parameters) do not strongly influence rate of CO<sub>2</sub> trapping.

293

#### 294 *4.2. Test for N<sub>2</sub>O interference in $\delta^{13}C$ measurement*

295

296 Samples of atmospheric CO<sub>2</sub> recovered using the molecular sieves showed no  
297 significant difference in  $\delta^{13}C$  before and after passing through Cu at 650 °C (Table 3).  
298 In contrast, a sample of soil respiration collected using an evacuated flask did show a

299 significant positive shift of 0.6 ‰ after Cu treatment, implying interference from N<sub>2</sub>O.  
300 However, a passive MSC sample collected from the same soil chamber did not show a  
301 significant change in δ<sup>13</sup>C after processing through heated Cu. The results therefore  
302 suggest that N<sub>2</sub>O does not cause a significant interference in the measurement of δ<sup>13</sup>C  
303 of samples collected using the MSCs. Although Godbout et al. (2006) have shown  
304 that zeolite molecular sieve can trap N<sub>2</sub>O, they used a different type of zeolite (5A).  
305 Kuc (1991) stated that it is probable that N<sub>2</sub>O decomposes during heating of the  
306 molecular sieves (i.e. during discharging), and therefore does not form part of the  
307 cryogenically purified CO<sub>2</sub> sample.

308

#### 309 *4.3. Sampling of atmospheric CO<sub>2</sub>*

310

311 We found significant strong linear correlations between volume of CO<sub>2</sub> recovered and  
312 exposure time for MSCs sampling the free atmosphere (Fig. 3). Rate of CO<sub>2</sub> trapping  
313 was 3-4 times greater in the ‘two openings’ configuration compared to the ‘one  
314 opening’ mode. Fick’s law states that trapping rates should be dependent on the total  
315 cross sectional area of the sampling cartridge (equation 2). The 2<sup>nd</sup> opening, employed  
316 only in the ‘two openings’ configuration, was much wider than the first, which  
317 explains why the trapping rate increased by more than a factor of 2.

318

319 Atmospheric CO<sub>2</sub> concentration can vary locally over daily and seasonal cycles, and  
320 therefore the rate of CO<sub>2</sub> trapping would vary correspondingly. This might explain  
321 some of the scatter in the relationship between volume of CO<sub>2</sub> recovered and exposure  
322 time (Fig. 3). To negate this issue, and still test that the MSCs recovered  
323 representative samples, we adopted a sampling design whereby cartridges were

324 exposed concurrently, but for different lengths of time; if representative samples were  
325 collected, the combined results from short period samples should provide identical  
326 results to single samples collected over the same time period.

327

328 For both configurations, in almost all cases the volume recovered from the shorter  
329 period samples was within measurement uncertainty of the corresponding longer  
330 period sample (Tables 1 and 2). This implies that the MSCs collected representative  
331 volumes of CO<sub>2</sub> no matter what the exposure time. Similarly, the average  $\delta^{13}\text{C}$  values  
332 of shorter period samples were in almost all cases within measurement error of the  
333 longer period sample, again suggesting that length of sampling time did not affect the  
334  $\delta^{13}\text{C}$ . However, there was one exception. In the ‘two openings’ configuration, the  
335 volume of CO<sub>2</sub> recovered from the long period sample was considerably less than  
336 expected based on summing the two medium period samples (Table 2). We consider  
337 that the likely explanation is that the long period sample became saturated with water,  
338 due to progressive adsorption of atmospheric H<sub>2</sub>O. From previous work (Garnett et  
339 al., 2009) we know that the zeolite in the MSCs has the capacity to trap well over 100  
340 ml of CO<sub>2</sub>, and therefore CO<sub>2</sub> saturation is unlikely. Although, the hydrophobic filters  
341 prevented the entry of liquid water into the cartridge, they do not stop water vapour,  
342 and Type 13X molecular sieve preferentially adsorbs H<sub>2</sub>O over CO<sub>2</sub> (and anything  
343 else; Hardie et al., 2005). H<sub>2</sub>O will have been far more abundant in the atmosphere  
344 than CO<sub>2</sub> during sampling (especially since sampling was performed from autumn to  
345 winter within a temperate/oceanic climate). It therefore seems likely that at some  
346 stage during sampling, adsorption of water vapour by the MSC became so great that  
347 this reduced the capacity of the zeolite available to trap CO<sub>2</sub>. In addition, due to  
348 preferential adsorption of H<sub>2</sub>O, some CO<sub>2</sub> already trapped on the MSC was probably

349 displaced, further reducing the volume of trapped CO<sub>2</sub>, and resulting in isotopic  
350 fractionation as the lighter <sup>12</sup>CO<sub>2</sub> was preferentially displaced. This explains the  
351 increased δ<sup>13</sup>C of the CO<sub>2</sub> remaining on the zeolite (Table 2).

352

353 Preferential adsorption of water by zeolite in the MSCs is a potential problem.

354 Although the extent of the problem will depend on the conditions under which the  
355 MSCs are deployed, we only found evidence of this problem in the long period MSC  
356 exposed for 168 days in the ‘two openings’ configuration. Our results therefore imply  
357 that representative samples with sufficient volumes of CO<sub>2</sub> for <sup>14</sup>C analysis can be  
358 collected at ambient atmospheric CO<sub>2</sub> concentrations over a period of between ~160  
359 to 300 days in the ‘one opening’ configuration, and between 40 and at least 84 days  
360 (but less than 168 days; depending on humidity levels) in the ‘two openings’ mode.

361

#### 362 *4.4. Correcting δ<sup>13</sup>C ratios for isotopic fractionation*

363

364 All passively collected molecular sieve samples were <sup>13</sup>C-depleted compared to  
365 pumped samples. It was shown by Hardie et al. (2005) that no isotopic fractionation  
366 occurs when the MSCs are used to trap CO<sub>2</sub> using a pump-based method, and in the  
367 present study the δ<sup>13</sup>C of pump-based samples are similar to the expected δ<sup>13</sup>C of  
368 atmospheric CO<sub>2</sub> (Hemming et al., 2005). The discrepancy in δ<sup>13</sup>C values is most  
369 likely due to isotopic fractionation during passive sampling as reported previously for  
370 both molecular sieves (Garnett et al., 2009) and CO<sub>2</sub> absorption by hydroxide  
371 (Davidson, 1995).

372



373 Samples of atmospheric CO<sub>2</sub> collected passively had a δ<sup>13</sup>C ranging from -13.0 to -  
374 14.2 ‰ (excluding the ‘two openings’ long period sample for reasons outlined above),  
375 whereas pumped samples ranged from -8.5 to -11.4 ‰. However, over the course of  
376 the sampling, the δ<sup>13</sup>C of the pumped samples varied by at least 3 ‰ (presumably  
377 reflecting changes in the contributions of plant/soil respiration and fossil-fuel derived  
378 CO<sub>2</sub>). This limits our ability to precisely quantify fractionation in the field component  
379 of our experiment. However, to overcome this problem, in the laboratory barrel  
380 experiment, fixed atmospheres were sampled, and the δ<sup>13</sup>C ratios of passive samples  
381 were compared with those collected using an evacuated flask. The CO<sub>2</sub> collected  
382 passively was <sup>13</sup>C-depleted by an average of 4.16±0.25 ‰ (SD; n=6) relative to the  
383 evacuated flask samples, which is almost identical to a recent estimate of 4.0±0.2 ‰  
384 (SD n=4) for the fractionation effect by Garnett and Hardie (2009). Precise  
385 quantification of the level of fractionation involved in passive sampling allows the  
386 δ<sup>13</sup>C values to be corrected (Tables 1 and 2), giving a range for atmospheric CO<sub>2</sub>  
387 samples of -8.8 to -10.0 ‰, which corresponds closely to the pumped samples and the  
388 expected average δ<sup>13</sup>C of the free atmosphere. Therefore, the need to correct for  
389 fractionation only results in a slight increase in uncertainty in the δ<sup>13</sup>C results.  
390 Importantly, it should be emphasised that fractionation has no impact on <sup>14</sup>C  
391 measurements (the main aim of this technique), as these are routinely normalised to a  
392 δ<sup>13</sup>C of -25 ‰ when expressed as ‰modern (Stuiver and Polach, 1977).

393

#### 394 *4.5. Suitability for <sup>14</sup>C analysis*

395

396 The main aim of this study was to develop and test a method to passively sample  
397 atmospheric CO<sub>2</sub> for <sup>14</sup>C analysis. The testing involved comparison between samples

398 collected passively with those collected using the pumped-based method, as well as  
399 comparison between samples collected simultaneously over different time periods. A  
400 limiting factor was the volume of CO<sub>2</sub> recovered; although at our laboratory only 1-2  
401 ml of CO<sub>2</sub> is required for routine <sup>14</sup>C measurement, and δ<sup>13</sup>C analysis can be  
402 determined with as little as 0.1 ml, it is recommended that at least 5 ml of CO<sub>2</sub> is  
403 provided using the molecular sieve method due to the additional steps in processing  
404 these samples and resulting slightly higher <sup>14</sup>C background. Therefore, from the field  
405 experiment testing the ‘one opening’ configuration, only one passively collected  
406 sample was analysed for <sup>14</sup>C, while three samples of passively collected atmospheric  
407 CO<sub>2</sub> were analysed for <sup>14</sup>C using the ‘two opening’ configuration.

408

409 For the ‘one opening’ configuration, the long period sample had a <sup>14</sup>C concentration  
410 that was within measurement error (< 1 σ) of the two pumped samples collected at the  
411 start and end of the sampling period, and all values were close to the expected <sup>14</sup>C  
412 content of the contemporary atmosphere (~105.2 %modern; from extrapolating the  
413 record of Levin et al., 2008). In the ‘two openings’ configuration, the average <sup>14</sup>C  
414 content of the two short period samples was within measurement uncertainty (<2 σ) of  
415 the corresponding medium period sample collected at the same time (Table 2),  
416 implying that representative samples had been collected at the different lengths of  
417 exposure time. All three passively collected MSC samples from the ‘two openings’  
418 configuration were within measurement uncertainty (<2 σ) of the expected <sup>14</sup>C content  
419 of the contemporary atmosphere. We therefore consider that samples collected using  
420 passive molecular sieve sampling provided representative samples for <sup>14</sup>C analysis.

421

422 It was notable, however, that for the ‘two opening’ configuration, the pumped sample  
423 collected on day 84 was  $^{14}\text{C}$  depleted compared with all other samples. The most  
424 likely explanation is that this sample had a component of  $\text{CO}_2$  derived from fossil  
425 fuel. Even on regional scales atmospheric  $\text{CO}_2$  can be  $^{14}\text{C}$ -depleted due to  
426 contributions from fossil fuel combustion (Levin et al., 2008), whereas localised  
427 depletions of as much as 20 % have been reported (Baxter and Harkness, 1975).

428

429 The  $^{14}\text{C}$ -depleted value for the day 84 pumped sample highlights an important  
430 difference between the two sampling approaches. The pumped method allows samples  
431 to be collected within an hour, but they will be representative only of this short time  
432 period. In contrast, the samples collected passively require a much greater sampling  
433 time to provide sufficient  $\text{CO}_2$ . Clearly, the pumped method could be modified to  
434 permit collection of samples over longer time scales (e.g. reducing pump speed).  
435 Similarly, changes to the MSC design can be made to either increase or decrease the  
436 rate of  $\text{CO}_2$  trapping when used passively. For example, as predicted by Fick’s law,  
437 increasing the distance between the molecular sieve and the opening to atmosphere  
438 will decrease the rate of  $\text{CO}_2$  trapping. Pump-based systems can be used to study short  
439 term (hours to days) changes in the isotopic composition of atmospheric  $\text{CO}_2$ .

440 However, for long term  $^{14}\text{CO}_2$  monitoring (e.g. weeks to months) passive sampling  
441 has the advantages of integrating extended time periods, being very reliable and being  
442 capable of being deployed in remote locations as it does not require a power supply.

443

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445

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449 International Polar Year 2007-2008) from which this work arose.

450

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513 **Tables**

514

515 Table 1

516 Volume (ml  $\pm$  0.1 ml),  $\delta^{13}\text{C}$  (in brackets;  $\pm 0.1$  ‰ ( $1\sigma$ )) and  $^{14}\text{C}$  content (*italics*;

517 ‰modern) of atmospheric  $\text{CO}_2$  collected by passive trapping on molecular sieve

518 using the ‘one opening’ configuration of sampler. Samples were collected for

519 different exposure times: short (S; 42 or 84 days), medium (M; 126 or 168 days)

520 and long (L; 294 days). Sampling was concurrent so that sieve cartridges

521 experienced the same conditions, and therefore, where results from short period

522 samples have been combined they should be identical to results for the

523 corresponding longer period sample (see Fig. 2 and text). Radiocarbon publication

524 codes given in square brackets.

525

	<b>Days 1-42</b>	<b>Days 43-126</b>	<b>Days 127-210</b>	<b>Days 211-294</b>	<b>Total</b>
<b>S</b>	1.4 (-13.5)	2.8 (-13.3)	2.7 (-14.0)	2.4 (-13.5)	9.2 (-13.6)
<b>S (combined)</b>	4.1 (-13.4)		5.1 (-13.8)		9.2 (-13.6)
<b>M</b>	4.2 (-13.0)	5.3 (-13.8)			9.4 (-13.4)
<b>M (combined)</b>	9.4 (-13.4)				9.4 (-13.4)
<b>L</b>	8.7 (-13.3)				8.7 (-13.3)
	<i>104.49 <math>\pm</math> 0.49</i>				
	<i>[SUERC-18752]</i>				
<b>Pumped</b>	(-8.5)	(-9.3)	(-10.2)		(-9.3)
	<i>104.71 <math>\pm</math> 0.49</i>		<i>104.06 <math>\pm</math> 0.48</i>		
	<i>[SUERC-18741]</i>		<i>[SUERC-18753]</i>		

526

527 Table 2  
 528 Volume (ml  $\pm$  0.1 ml),  $\delta^{13}\text{C}$  (in brackets;  $\pm 0.1$  ‰ (1 $\sigma$ )) and  $^{14}\text{C}$  content (*italics*;  
 529 %modern) of atmospheric CO<sub>2</sub> collected by passive trapping on molecular sieve  
 530 using the ‘two openings’ configuration of sampler. Samples were collected for  
 531 different exposure times: short (S; 42 days), medium (M; 84 days) and long (L;  
 532 168 days). Sampling was concurrent so that sieve cartridges experienced the same  
 533 conditions, and therefore, where results from short period samples have been  
 534 combined they should be identical to the results for the corresponding longer  
 535 period sample (see Fig. 2 and text). Radiocarbon publication codes given in square  
 536 brackets.

	<b>Days 1-42</b>	<b>Days 43-84</b>	<b>Days 84-126</b>	<b>Days 127-168</b>	<b>Total</b>
<b>S</b>	5.1 (-13.3)	5.0 (-13.9)	<u>5.2 (-14.2)</u>	<u>4.3 (-14.2)</u>	19.6 (-13.9)
	<i>105.18 <math>\pm</math> 0.49</i>	<i>104.44 <math>\pm</math> 0.46</i>			
	[SUERC- 18743]	[SUERC- 18746]			
<b>S (combined)</b>	10.1 (-13.6)		9.5 (-14.2)		19.6 (-13.9)
	<i>104.81</i>				
<b>M</b>	9.6 (-13.5)		9.8 (-14.1)		19.4 (-13.8)
	<i>105.46 <math>\pm</math> 0.49</i>				
	[SUERC-18747]				
<b>M (combined)</b>			<u>19.4 (-13.8)</u>		19.4 (-13.8)
<b>L</b>		14.8 (-12.6)			14.8 (-12.6)
<b>Pumped</b>	(-9.0)	(-11.4)		(-10.8)	(-10.4)
	<i>105.82 <math>\pm</math> 0.46</i>	<i>101.37 <math>\pm</math> 0.44</i>			
	[SUERC-18742]	[SUERC-18748]			



537 Table 3  
 538  $\delta^{13}\text{C}$  of cryogenically purified  $\text{CO}_2$  before and after heating at  $650^\circ\text{C}$  in presence  
 539 of Cu. Given analytical uncertainty of the  $\delta^{13}\text{C}$  measurement ( $\pm 0.1\text{‰}$ ;  $1\sigma$ )  
 540 positive differences greater than  $0.4\text{‰}$  (\*) suggest significant presence of  $\text{N}_2\text{O}$  in  
 541 the original sample.

542

543

<b>Material</b>	<b>Sampling method</b>	<b><math>\delta^{13}\text{C}</math> (before Cu)</b>	<b><math>\delta^{13}\text{C}</math> (after Cu)</b>	<b>Difference</b>
Atmospheric $\text{CO}_2$	Pumped MSC	-9.5	-9.6	-0.1
Soil respired $\text{CO}_2$ A	Pumped MSC	-17.7	-18.0	-0.3
Soil respired $\text{CO}_2$ B1	Passive MSC	-30.1	-29.7	0.4
Soil respired $\text{CO}_2$ B2	Evacuated flask	-25.9	-25.3	0.6*

544

545 **Figure captions**

546

547 Fig. 1

548 Schematic diagram of MSC used for passive sampling of atmospheric CO<sub>2</sub> ('two  
549 openings' configuration). For 'one opening' configuration the right hand side  
550 coupling was closed and sealed using a clip.

551

552 Fig. 2

553 Experimental design. Three MSCs were sampling at any one time; one from each of  
554 the short (S), medium (M) and long (L) sampling periods. This design tests that  
555 cartridges trap representative samples of CO<sub>2</sub> for different exposure lengths, even if  
556 the concentration and isotopic characteristics of atmospheric CO<sub>2</sub> varies; the  
557 combined results from shorter period samples should equal values for the  
558 corresponding longer period samples (see text). P1, P2 and P3 samples collected at  
559 three time points over the course of the sampling period using a pump-based sampling  
560 system.

561

562 Fig. 3

563 Volume of CO<sub>2</sub> recovered from each MSC plotted against length of exposure time.  
564 Regression lines are based on the full set of results for both experiments, except for  
565 dashed line which represents the regression when long period sample from the 'two  
566 opening' configuration was removed. All three correlations were highly significant  
567 ( $P < 0.001$ ).

568

569 Fig. 4

570 Rate of CO<sub>2</sub> trapping by passive molecular sieve sampling ('one opening'  
571 configuration) against CO<sub>2</sub> concentration of atmosphere. Squares represent results for  
572 six samples collected from a 30 L closed chamber at three CO<sub>2</sub> concentrations, and  
573 dashed line represents regression (line forced through origin;  $P < 0.001$ ). Full line  
574 represents theoretical relationship between trap rate and CO<sub>2</sub> concentration based on  
575 Fick's Law, for the 'one opening' configuration of MSC (see text).  
576

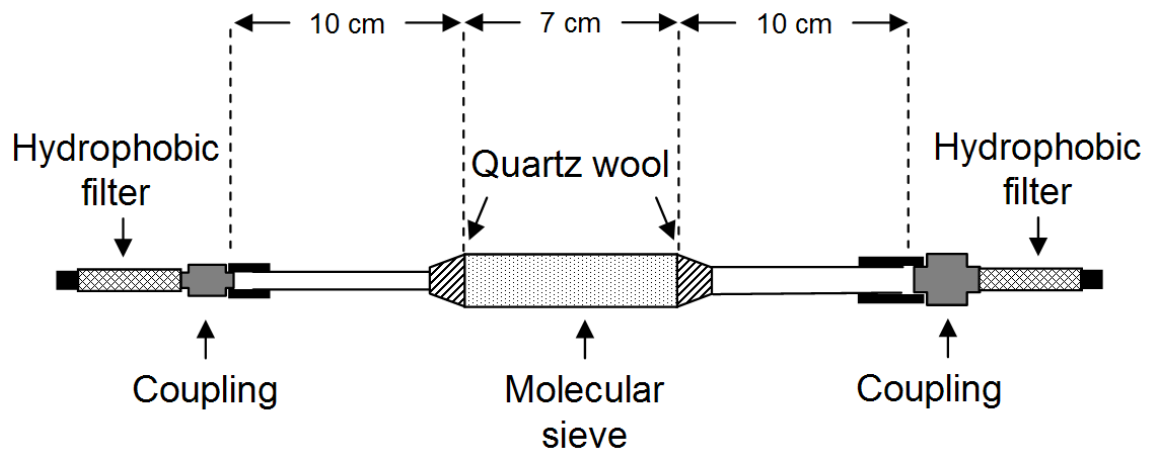
577 Fig. 1

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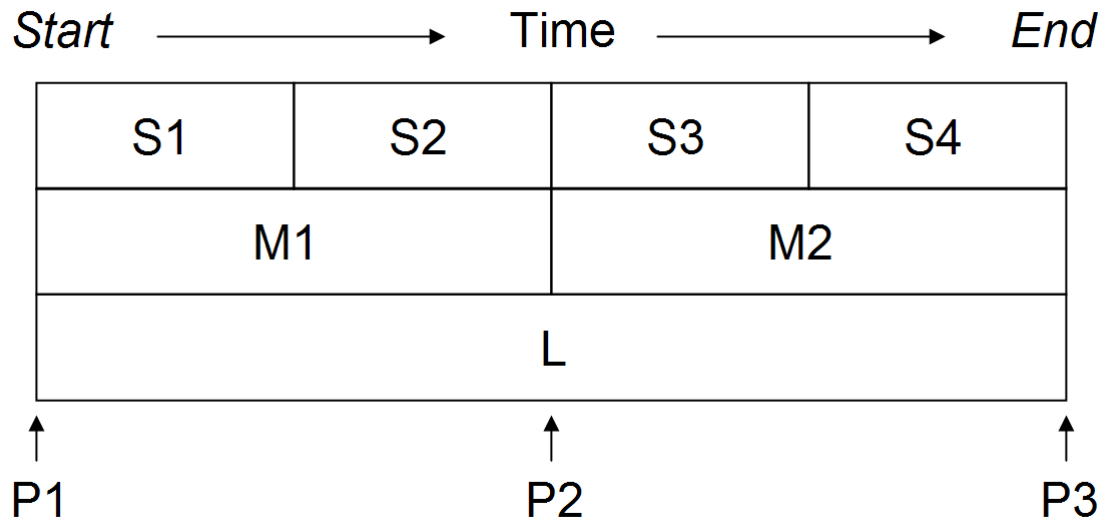


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Fig. 2

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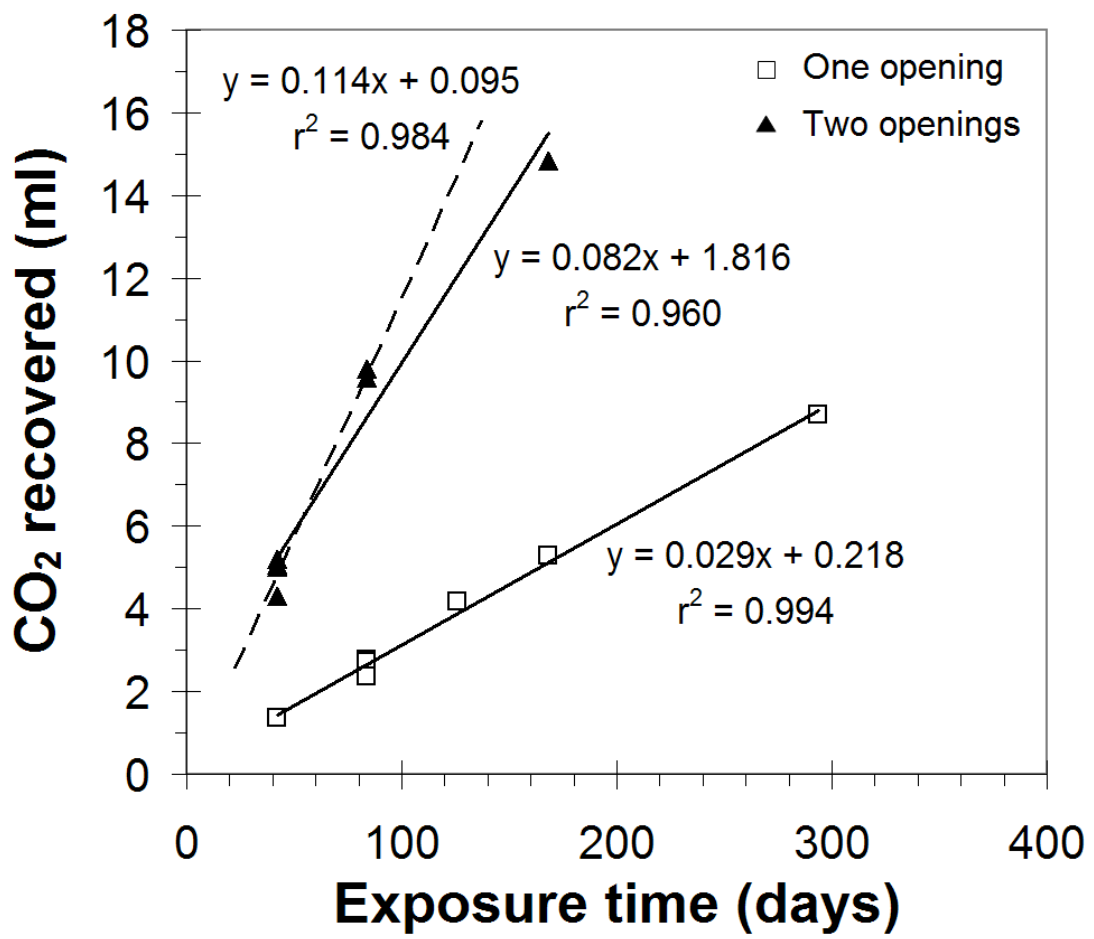


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Fig. 3

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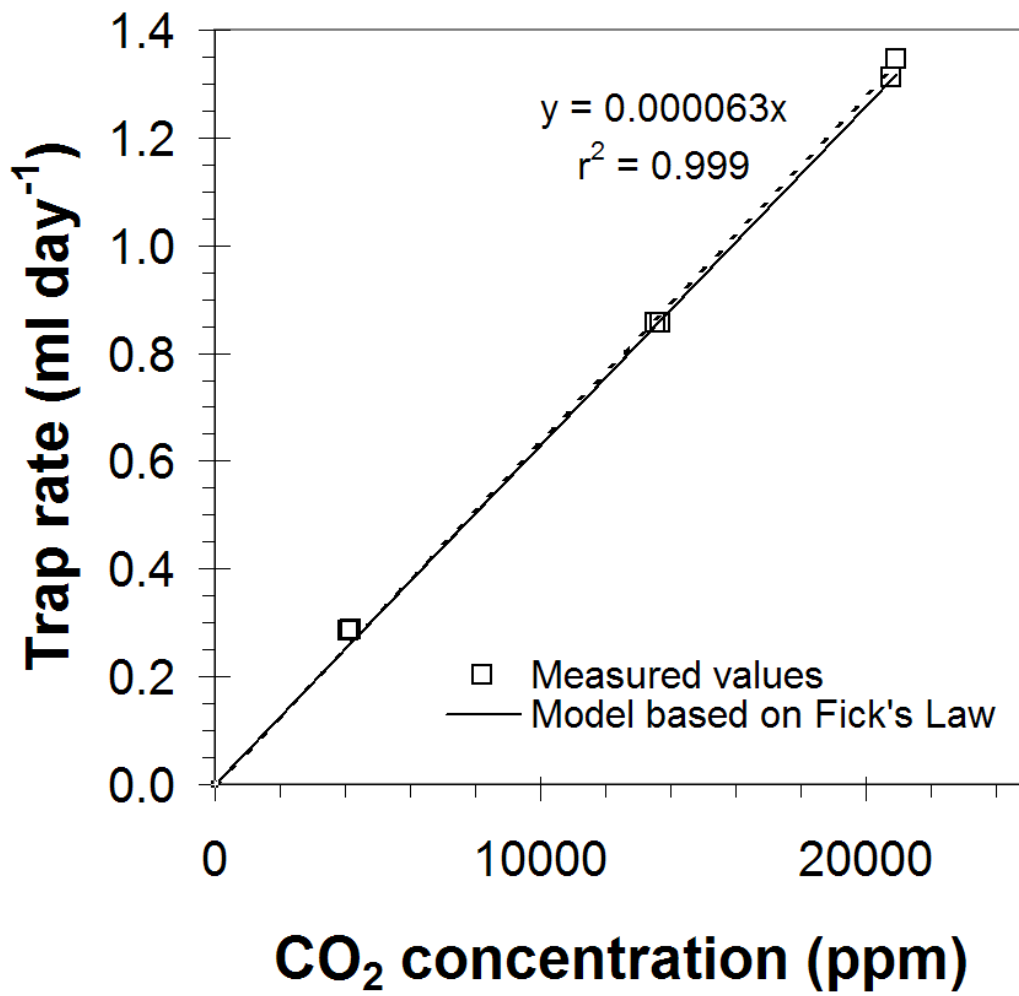
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Fig. 4

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