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LOW-FLOW PRESSURE GRADIENT PUMPING FOR ACTIVE ABSORPTION OF CO_2 ON A MOLECULAR SIEVE

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ABSTRACT. The authors have developed an active absorption system combining a molecular sieve with a pressure gradient as a way to overcome the shortcomings of the phosphoric acid solution displacement method. Taking advantage of the pressure gradient produced between the inside and outside of a bottle, as water moves through it, CO_2 in the atmosphere can actively be absorbed onto a molecular sieve in its pathway. A comparative study showed that the technique was in agreement with the phosphoric acid displacement method, within error. We applied the new method to collect not only atmospheric CO_2 samples, but also CO_2 samples from soil respiration to verify its utility. Simple yet practical, our method is well suited to extended collection times in a variety of environments, and capable of providing relatively large amounts of carbon for high-precision accelerator mass spectrometry (AMS) ^{14}C analyses of atmospheric samples.

KEYWORDS: molecular sieve, active absorption, ^{14}C, atmospheric CO_2.

INTRODUCTION

Fossil fuel combustion comprises the largest anthropogenic CO_2 source on Earth. It accounted for approximately 7.0 GT yr^{-1} in 2000, and increased rapidly to over 9.8 GT yr^{-1} in 2014 (Marland et al. 2006; Raupach et al. 2007; Le Quéré et al. 2015). From 1870 to 2014, approximately 400 GT of carbon were released to the atmosphere from the consumption of fossil fuels and cement production (Le Quéré et al. 2015). This accelerated trend began centuries ago and the mole fraction of atmospheric CO_2 has been steadily increasing since the Industrial Revolution (IPCC 2007). Therefore, monitoring atmospheric CO_2 sources is increasingly important in the interests of establishing controllable strategies and implementing greenhouse gas regulations (Djuricin et al. 2007).

The radiocarbon concentration of atmospheric CO_2 can provide valuable information about its sources (Levin and Hesshaimer 2000; Takahashi et al. 2002; Kuc et al. 2003; Levin et al. 2003, 2008; Turnbull et al. 2006; Levin and Karstens 2007; Levin and Rodenbeck 2008). CO_2 from the combustion of fossil fuels contains no ^{14}C because the half-life of ^{14}C (5700 ± 30 yr) is much less than the age of fossil fuels. The difference between the ^{14}C compositions of CO_2 derived from fossil fuels (CO_{2ff}) and from modern CO_2 sources is large, and this contrast makes ^{14}C a unique and sensitive tracer in the atmosphere (Levin et al. 1989, 2003; Levin and Hesshaimer 2000; Turnbull et al. 2006; Hsueh et al. 2007; Kuc et al. 2007; Zhou et al. 2014).

Currently, several liters of air are needed to extract enough CO_2 for a high-precision accelerator mass spectrometry (AMS) ^{14}C measurement. AMS can measure ^{14}C in much smaller samples, but high-precision measurement is needed for atmospheric studies. Suitable samples can be collected using flasks or gas sample bags. However, these collection methods provide a sample that is only representative of one point in time. It can be argued that for the atmospheric measurement, a better sampling strategy would be to collect samples representative of longer time periods (Garnett and Hartley 2010). This can be achieved by slowly pumping air through a medium that can extract CO_2, for example, using a molecular sieve or absorption in an alkaline solution such as sodium hydroxide (Dörr and Münnich 1986; Bauer et al. 1992; Bol and Harkness 1995; Gaudinski et al. 2000; Koarashi et al. 2002; Hardie et al. 2005; Palonen 2015).

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Other alternatives include the use of passive samplers (Garnett et al. 2009; Garnett and Hartley 2010; Walker et al. 2015) or differential pressure gradient samplers, which utilize the physical displacement of a solution of phosphoric acid (Zhou et al. 2014). These passive methods have the advantage that they require no external energy supply.

Air samples at the Institute of Earth Environment, Chinese Academy of Sciences (IEECAS) in Xi'an (34°13′37.97″N; 109°0′42.30″E) were collected from 2011 to 2013 using a time-integrated sampling technique we developed, which we refer to as the phosphoric acid solution displacement method (Zhou et al. 2014). The addition of phosphoric acid to water prevents the dissolution of atmospheric CO_2 during sampling, which is in contact with the displacement solution, from equilibrating and exchanging CO_2 with the solution, which could lead to contamination or offsets. However, there are two shortcomings. The first is that an acid solution, which is corrosive, must be prepared for each sample and cannot be recycled. The second is the limitation caused by the 4000-mL glass bottle used to preserve CO_2 being more fragile for long-distance transportation. For these reasons, we developed an active absorption system using a molecular sieve with the pressure gradient produced by the water flowing out of a glass bottle, drop by drop. This method is beneficial because no electricity or dangerous chemicals are required and CO_2 can be actively absorbed slowly into the sieve, with an integrating period from hours to weeks. Our method makes it possible to sample in the extreme weather, such as heavy rain or snow. In addition, after sampling, we can renew the new molecular sieve cartridge to continue sampling. It is more convenient to send the molecular sieve cartridge with CO_2 to the lab by post.

METHODS

Sampling System Design

The CO_2 sampling device is composed of two parts (Figure 1): (1) a molecular sieve device and (2) pressure gradient apparatus. The molecular sieve device includes a molecular sieve cartridge (MSC), which is a modification of the one previously described by Hardie et al. (2005) and Garnett et al. (2009), and desiccator as shown in Figure 2.

The MSC was made in a quartz tube and the center of cartridge [12 mm outside diameter (OD), 60 mm length] was filled with 5 g of 13X molecular sieve (1/16″ pellets, Pingxiang Naike Chemical Industry Equipment Packing Co., Ltd, China), and secured with quartz wool at the ends. Typically, 100 g of the 13X sieve has the capacity to store ~0.5 g of CO_2 (Giacobbe 1991). In practice, more sieve is selected to ensure successful collections; thus, 5 g were used in this paper. Both ends of each cartridge (9 mm OD, 120 mm length) were sealed by two auto-shutoff Quick Couplings (Colder Products Company, USA) attached via short lengths of tubing (Tygon, Fisher, UK). When not mated to other couplings, the couplings on the MSC automatically sealed and a clip was placed across the tubing to form an additional seal. During sampling, one end of the MSC was attached with the quick coupling placed on the pump of the CO_2 sampling device, and the other end of the MSC was attached with the desiccator constructed using a glass tube (18 mm OD, 100 mm length) filled with $CaCl_2$ (AR, 1–2 mm pellets, Beijing Chemical Industry Co., Ltd, China), as shown in Figure 2.

The pressure gradient apparatus consisted of an 8000-mL custom-made glass bottle with a water flow regulator at the bottleneck, with a 9-mm-OD, 60-mm-long glass tube attached to the bottle (Figure 1). This device is designed to actively absorb CO_2 from the atmosphere. The water pressure induces a gradient between the inside and outside of the bottle, driven by the water flowing out of the glass bottle, drop by drop. Atmospheric CO_2 is actively absorbed onto the molecular sieve. The flow rate can be controlled by a regulator to meet a targeted sampling

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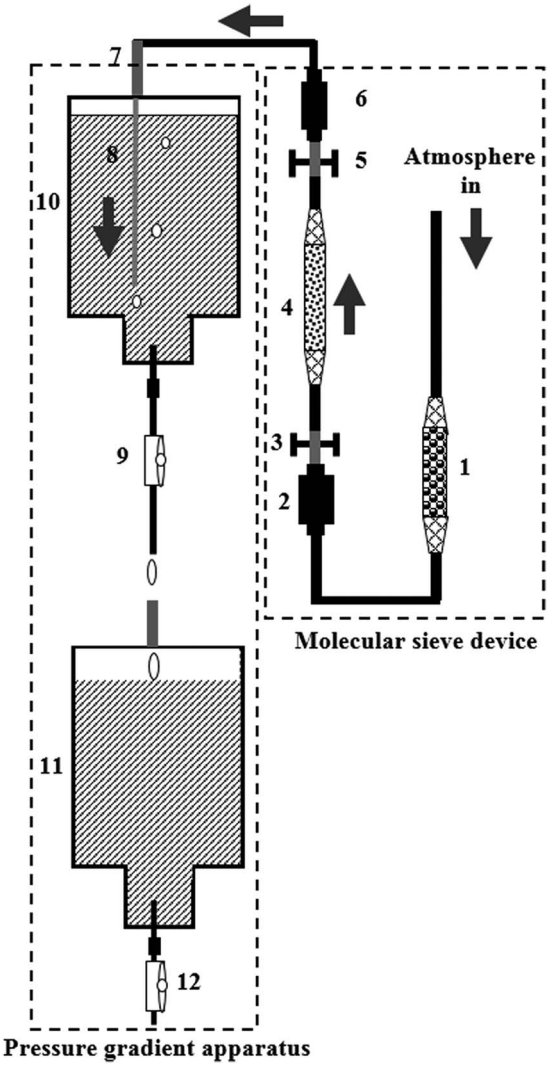


Figure 1 Schematic illustration of the CO_2 sampling device: (1) desiccator; (2) quick coupling; (3) clip; (4) molecular sieve cartridge (MSC); (5) clip, (6) quick coupling; (7) glass tube; (8) silicone tubing; (9) flow regulator; (10) glass bottle 1; (11) glass bottle 2; (12) flow regulator.

duration (e.g. hours, days, or weeks). In addition, the dripping water can be collected in a separate glass bottle for reuse as shown in Figure 1.

Before sampling, we ensure that an adequate pressure gradient is achieved using the following steps (with numbered references to Figure 1):

1. Place an 8000-mL glass bottle on the support, close the flow regulator (9), and insert a 5-mm-OD, 200-mm-long silicon pipe (8), which extends from an upper glass tube (7) to the bottom of the first glass bottle (10).

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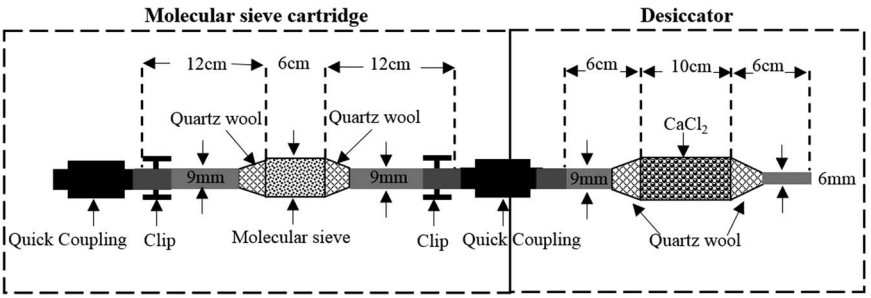


Figure 2 Schematic diagram of the molecular sieve device

2. Link the MSC (4) with the glass tube (7) using the quick coupling (6), and connect the quick coupling (2) with one side of the desiccator tube (1), then open clips (3) and (5).
3. Seal the air intake of the desiccator tube (1), and maximize the flow regulator (9) to initiate water flow. Wait about 30 s. When the dripping stops, a pressure gradient has been achieved.
4. Open the air-intake of the desiccator tube (1), adjust the flow regulator to the desired rate (9), and begin sampling.
5. If the water in the glass bottle (10) runs out, replace the glass bottle (11) to continue sampling, and repeat the procedure above until meeting the targeted sampling duration.
6. When finished, remove the molecular sieve device (4), and insert it into a furnace to liberate CO_2.

Molecular Sieve Cartridge Activation and Desorption

We designed a 60-mm-OD × 250-mm-long muffle tube furnace, with a zone of uniform temperature of about 150 mm. In the center of this tube furnace, there is a zone of uniform temperature that extends to about 2.5 times the diameter of the tube measured from the outside of the furnace (Hardie et al. 2005). We introduced a quartz cartridge with molecular sieve (MSC), which is 12 mm OD, 60 mm length. The length of uniform temperature within the muffle furnace can assure complete sample recovery when desorbing the molecular sieve.

The MSC should be activated completely before sampling to ensure that it is free of contamination. Prior to inserting the MSC into a tube furnace, one side was connected to a source of high-purity N_2. The MSC was then inserted into a tube muffle furnace and heated to 550°C, and high-purity (99.999%) N_2 was passed through the sieve at a rate of 180 mL/min for at least 20 min (Figure 3). The MSC was allowed to cool to <30°C and filled with high-purity N_2 gas at a pressure slightly above atmospheric (~1100 mbar). We also noted a minor amount of hysteresis that cannot absorb CO_2 completely in the molecular sieves on their first use. The fresh molecular sieve was first purged of all gases and then flushed with CO_2 in an air stream and repurged prior to sampling (Hardie et al. 2005).

The following steps were followed to desorb the CO_2 from the sample cartridges after sampling (with reference to Figure 3). The MSC was inserted into a tube furnace and attached to a vacuum with a quick coupling and evacuated to less than 10^{-2} Torr. The connections leading up to the cartridge were then evacuated. Cold trap 1 (–76°C) was cooled with a liquid nitrogen and alcohol mixture for removing H_2O and other gases, while cold trap 2 (–196°C)

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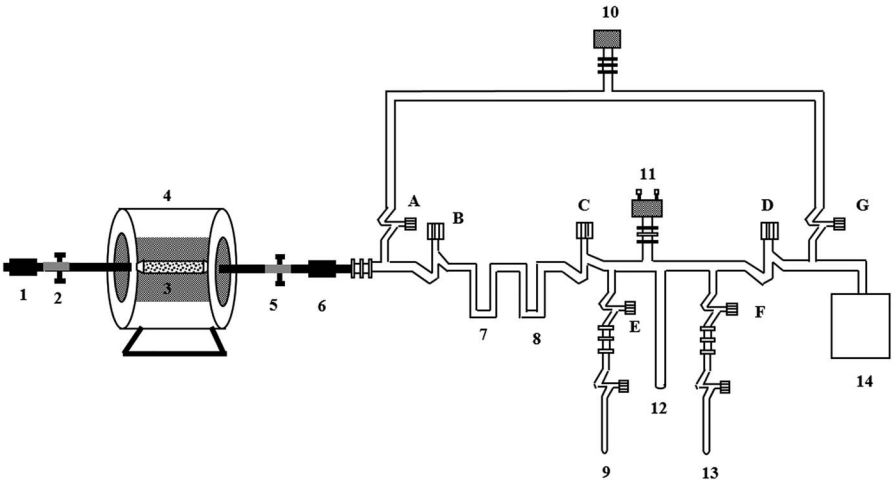


Figure 3 Schematic illustration of the MSC desorption: (1) quick coupling; (2) clip; (3) MSC; (4) tube furnace; (5) clip; (6) quick coupling; (7) cold trap 1; (8) cold trap 2; (9) gas collection unit; (10) vacuum gauge; (11) pressure transducer; (12) cold finger; (13) gas collection unit; (14) vacuum pump.

was cooled with liquid nitrogen for collecting CO_2 gas. The vacuum system was then isolated and the furnace temperature was raised to 550°C. CO_2 was collected at this temperature under a static vacuum for 20 min. Non-condensable gases were pumped away after a vacuum of 10^{-2} Torr was achieved in the system. The CO_2 was transferred to a calibrated volume between valves C and D, and the pressure of the gas was measured using a pressure transducer (Type 660, MKS, USA) to determine the amount of CO_2 collected. A portion of the CO_2 was reduced to graphite with a Zn/Fe catalytic reduction (Slota et al. 1987; Jull 2007) for the AMS analysis. The AMS measurements were performed with a 3MV tandem accelerator at the Xi'an AMS Centre, Xi'an, China (Zhou et al. 2006). A second portion of the CO_2 sample were measured for ^{13}C by a Thermo Finnigan DELTA plus XL isotope ratio mass spectrometer in the Institute of Earth Environment, Chinese Academy of Sciences (IEECAS).

DISCUSSION

Test of Laboratory Methods

A total of six CO_2 gas samples were used to test the recovery rate onto the molecular sieve. Each gas sample was divided into two equal C mass portions. One portion of the CO_2 was directly converted into graphite for ^{14}C measurement, while another portion of the CO_2 was used for molecular sieve absorption and desorption (MSAD), described by our methods above, and the recovered CO_2 was converted into graphite for AMS ^{14}C analysis. AMS results are expressed as fraction of modern carbon (F) values, defined following Donahue et al. (1990).

We observed a recovery rate of 96–97% for the customized tube furnace at a temperature of 500°C and collection time of 20 min, and repeated $F^{14}C$ values were beyond errors at the 2σ level. Sample recovery was improved (to 99%) by increasing the desorption temperature to 550°C (Table 1). These parameters also gave good reproducibility at the 2σ level, so these conditions were adopted for routine sampling.

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Table 1 Results of mass and F ^{14}C without MSAD and with MSAD

Sample code	Method	Temp./Time	C/mg	Recovery rates (%)	Lab code	$F^{14}C$	Uncertainty
FZS-1	No MSAD		0.80		XA8404	0.9899	0.0037
	MSAD	500°C, 20 min	0.77	96	XA8405	0.9348	0.0029
FZS-2	No MSAD		1.15		XA8569	1.0542	0.0033
	MSAD	500°C, 20 min	1.11	97	XA8864	1.0417	0.0027
FZS-3	No MSAD		1.20		XA8392	0.1018	0.0011
	MSAD	550°C, 20 min	1.19	99	XA8393	0.1035	0.0012
FZS-4	No MSAD		1.46		XA8856	0.9645	0.0027
	MSAD	550°C, 20 min	1.45	99	XA8855	0.9600	0.0027
FZS-5	No MSAD		1.70		XA8400	1.0883	0.0034
	MSAD	550°C, 20 min	1.69	99	XA8406	1.0824	0.0044
FZS-6	No MSAD		1.25		XA8565	0.9415	0.0024
	MSAD	550°C, 20 min	1.25	99	XA8850	0.9434	0.0024

Comparison with the Phosphoric Acid Solution Displacement Method

We collected atmospheric samples from the same locality at the same time for a comparative study. All of the ^{13}C values are reported using the delta notation with $^{13}C/^{12}C$ variations relative to the international standard Vienna Pee Dee Belemnite (VPDB). The ^{14}C results are reported as fraction modern carbon (F) values (Donahue et al. 1990).

Figure 4 and Table 2 show good overall reproducibility between the two methods at the 2σ uncertainty level. There is evidence for a small systematic difference in sample 5, both for ^{13}C (~1‰) and ^{14}C (~1%); however, the overall agreement is very consistent, so we consider both methods viable for sampling.

APPLICATION EXAMPLES

Atmospheric CO_2 Sample Collection

We collected atmospheric samples over about a 3-month period (15 September to 16 December 2013). Samples of atmospheric CO_2 were taken from the roof of the Xi'an AMS building. Xi'an's elevation is 440 m above sea level. The results are given in Table 3.

When the flow rate was less than 3 mL/min, as the water volume in the glass bottle gradually decreased, it stopped dripping. When the flow rate was more than 3 mL/min, it changed slightly as the water volume decreased, we were able to keep the flow rate as 3 mL/min by using a water flow regulator. The flow regulator was adjusted to around 3 mL/min, indicating water in an 8000-mL glass bottle will run out within 2 days. After 2 days, we renewed the glass bottle to continue sampling until we meet the targeted sampling duration. ^{14}C results are reported as $\Delta^{14}C$ values (Stuiver and Polach 1977), see Table 3.

CO_{2ff} values were calculated with the following equation (Levin et al. 2003; Kuc et al. 2007; Zhou et al. 2014):

$$CO_{2ff} = \frac{CO_{2obs}(\Delta_{obs} - \Delta_{bg})}{\Delta_{ff} - \Delta_{bg}}$$

where Δ_{ff} is –1000‰, Δ_{obs} is the $\Delta^{14}C$ of the air samples, and Δ_{bg} is the $\Delta^{14}C$ of the atmospheric background site.

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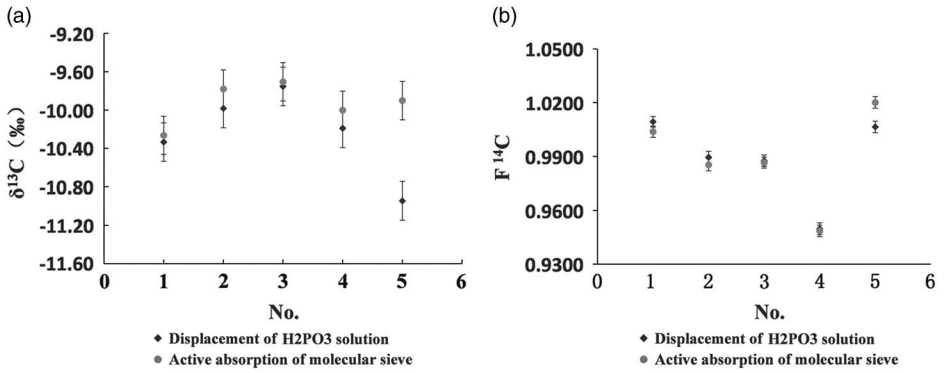


Figure 4 Comparison between the phosphoric acid solution displacement method and active absorption on a molecular sieve: (a) $\delta^{13}C$ results of the two methods, (b) $F^{14}C$ results of the two methods.

Table 2 $\delta^{13}C$ and F ^{14}C results of the two methods.

Sample code	$\delta^{13}C$ (±0.1‰)	Lab code	$F^{14}C$	Uncertainty
PSXH-1	–10.33	XA13645	1.0094	0.0029
FZSXH-1	–10.26	XA13646	1.0038	0.0031
PSXH-2	–9.98	XA14117	0.9895	0.0033
FZSXH-2	–9.78	XA14121	0.9853	0.0034
PSXH-3	–9.75	XA14128	0.9876	0.0032
FZSXH-3	–9.71	XA14112	0.9865	0.0031
PSXH-4	–10.19	XA12475	0.9498	0.0033
FZSXH-4	–10	XA13289	0.9485	0.0032
PSXH-5	–10.95	XA12673	1.0065	0.0032
FZSXH-5	–9.9	XA12678	1.0201	0.0032

Note: PSXH represents the displacement of H_3PO_4 solution method, and FZSXH represents active absorption of molecular sieve by pressure gradient from the water process.

For air samples, CO_{2obs} was derived by averaging continuously measured CO_2 data using a Picarro G2131-i CO_2 Carbon Stable Isotope Analyzer. The CO_2 mole fraction was measured about once a second at the $^{14}CO_2$ sampling site of the Institute of Earth Environment, Chinese Academy of Sciences (IEECAS), with a precision of 0.1 ppm.

Figure 5 shows that fossil fuel emissions were on the rise from September to December, with an average increase of ~0.4 ppm per day. We attribute this to the enhancement of coal burning for heating. The available ^{14}C measurement precision decreases with decreasing sample size. Our collection method has an average absorption rate of 1.0 mg C/day, much greater than that of passive absorption rates (e.g. 0.044 to 0.065 mg C/day, Walker et al. 2015). Over a 5-day integration period, our method is able to capture sufficient carbon for high-precision ^{14}C AMS, necessary for fossil-fuel apportionment studies.

Soil Respiration CO_2 Collection

Two MSCs were used for collecting respired CO_2 from a disturbed soil and a grassland for 6 and 12 hr, respectively. When the flow rate is more than 20 mL/min, there is no obvious change as

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Table 3 Atmospheric $CO_2\Delta^{14}C$ results for September 15 to December 16.

Lab code	Sample code	Sampling time (month/day)	CO_2 concentration (ppm)	Sampling period length (days)	$\Delta^{14}C$ (‰)	Uncertainty (‰)
XA9184	FYFZS-1	9/15–9/19	420	5	–12.41	2.53
XA9187	FYFZS-2	9/19–10/1	436	13	–13.22	2.6
XA9043	FYFZS-3	10/1–10/13	461	13	–28.64	4.43
XA9073	FYFZS-4	10/13–10/17	463	5	–79.60	3.39
XA9074	FYFZS-5	10/17–10/25	437	9	–71.63	3.39
XA9075	FYFZS-6	10/25–10/29	455	5	–70.32	3.54
XA9053	FYFZS-7	10/29–11/2	461	5	–43.73	3.73
XA9054	FYFZS-8	11/2–11/6	466	5	–55.57	3.41
XA9059	FYFZS-9	11/6–11/10	437	5	–61.77	3.74
XA9060	FYFZS-10	11/10–11/14	458	5	–56.21	3.55
XA9191	FYFZS-11	11/14–11/18	480	5	–60.16	2.82
XA9071	FYFZS-12	11/18–11/26	460	9	–44.07	3.73
XA9193	FYFZS-13	11/26–11/30	440	5	–39.91	2.42
XA9044	FYFZS-14	11/30–12/4	471	5	–87.76	3.44
XA9045	FYFZS-15	12/4–12/8	464	5	–98.24	3.54
XA9192	FYFZS-16	12/8–12/12	457	5	–88.73	2.11
XA9450	FYFZS-17	12/12–12/16	502	5	–115.34	2.71

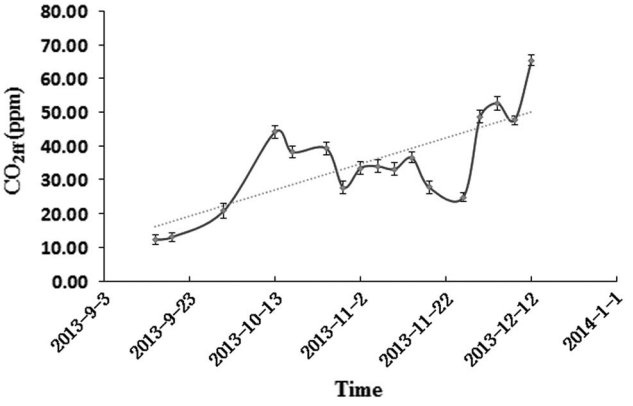


Figure 5 Trend of fossil fuel CO_2 mole fraction with time

the water volume decreases. The flow regulator was then adjusted to around 20 mL/min. When the water in the glass bottle ran out, we renewed the glass bottle to continue sampling until 12 hr had passed.

First, we pumped out the air from 8000-mL glass chamber for 10 min, then stopped pumping, waited for 1 hr so that CO_2 from soil respiration would fill in a glass chamber, and we then connected the chamber to the inlet of the CO_2 collection (Figure 6).

The results in Table 4 show that the $F^{14}C$ for the disturbed soil and grassland had no statistical difference found for each site for the 6-hr and 12-hr integration time. Therefore, the method seems very suitable for taking soil gas samples.

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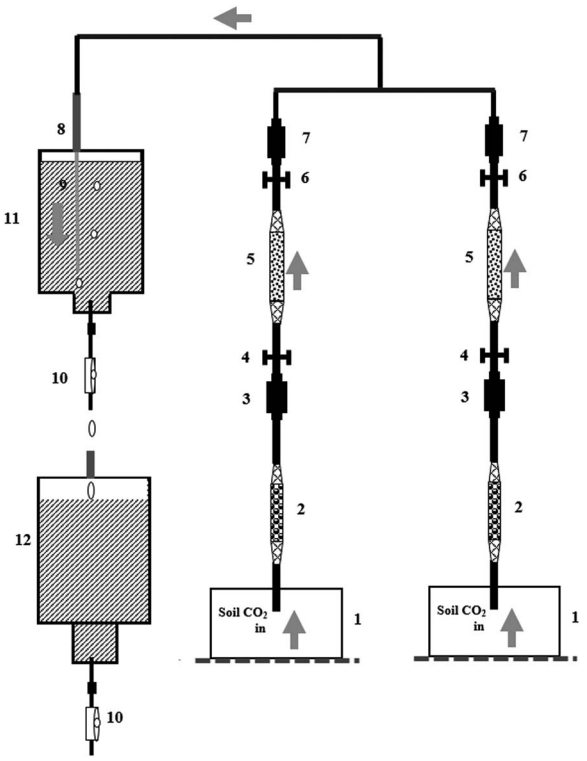


Figure 6 Schematic illustration of the soil respiration CO_2 collection: (1) glass chamber; (2) desiccator; (3) quick coupling; (4) clip; (5) MSC; (6) clip; (7) quick coupling; (8) glass tube; (9) silicone tube; (10) flow regulator; (11) glass bottle 1; (12) glass bottle 2.

Table 4 $F^{14}C$ results collected from different soil types.

Type of soil	Lab code	Time (hr)	$F^{14}C$	Uncertainty
Disturbed soil	XA8879	6	0.9944	0.0025
	XA8880	12	0.9936	0.0033
Grassland	XA8881	6	0.9876	0.0025
	XA8865	12	0.9868	0.0026

CONCLUSION

Our method makes use of a pressure gradient produced between the inside and outside of a bottle while water is a flowing through it, one drop at a time. This allows us to continually absorb CO_2 into a molecular sieve to collect a sufficient quantity for high-precision AMS ^{14}C measurements. We describe a customized tube muffle furnace used to desorb the CO_2 in the laboratory. We find that a desorption temperature of 550°C for at least 20 min is optimal, yielding recovery rates above 99% with good reproducibility. A comparison study of our method with our phosphoric acid solution displacement method gave comparable ^{13}C and ^{14}C results, and as the molecular sieve technique avoids the use of handling dangerous acid in the field, we see this as a distinct advantage. For atmospheric CO_2 sampling, the average absorption

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rate was 1.0 mg C/day by this method, which allows for high-precision AMS ^{14}C measurements. For soil CO_2 respiration sampling, our results showed that the $F^{14}C$ of a disturbed soil and a grassland showed no statistical difference for each site at the 6-hr and 12-hr integration time. The method thus seems very suitable for taking soil gas samples.

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